Modern Practice In Leather Manufacture

BY

JOHN ARTHUR WILSON, Sc. D.

CONSULTING CHEMIST TO THE LEATHER INDUSTRIES

REINHOLD PUBLISHING CORPORATION 350 WEST FORTY-SECOND STREET, NEW YORK, U. S. A.

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Printed in the United States of America by International Textbook press, scranton, pa.

THIS BOOK IS AFFECTIONATELY DEDICATED TO THE MEMORY OF OTTO RÖHM AND JOSEPH TURNEY WOOD IN RECOGNITION OF THEIR GREAT CONTRIBUTIONS TO THE DEVELOPMENT OF KNOWLEDGE IN THE LEATHER INDUSTRY

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Preface

There is no reliable single source of information available to which one can turn to learn all the details of operation involved in making each of the many different types of leather and the fundamental principles underlying each operation, although the demand for such a source of information is tremendous. This is not surprising when one considers that the raw materials used by the tanner are among the most complex known to science, and that many of the chemical reactions occurring in the making of leather still baffle the minds of the best chemists of our time.

Although the leather industry has sometimes been looked upon in financial circles as backward because of its difficulties in operating profitably, actually it has been making real progress in scientific procedure. When the history of progress is written, it will be found that the leather industry ranks high in its fundamental contributions to knowledge.

At intervals in the course of progress, opportunities are afforded one who has the time and interest to pause and portray the new and higher level reached by the industry and thus to provide a source of information a little closer to the ideal source so much in demand. The writing of this book was undertaken as the result of such an opportunity, and the writer hopes that it will fill a real need within the industry as well as provide interesting and instructive reading to those not actively engaged in making leather.

The procedures for making some types of leather are given in minute detail so as to illustrate the fundamental principles involved in making all types of leather. Similar detailed descriptions were not possible for every type of leather because of lack of information or available space in the book. However, it is believed that the fundamental principles have been sufficiently well covered to assist an experienced tanner to work out for himself the details of operation necessary to make any of the more important types of leather in common use.

An attempt has been made in writing this book to apportion space to each subject in proportion to its importance and interest to the tanner, and to present what might be considered the minimum that a tanner should know to carry on his business successfully in modern times. It is valuable for a tanner to become familiar with the microstructure, composition and functions of the living skin and with the structure and physical properties or characteristics of leather and their dependence upon chemical composition and the various mechanical operations to which hides and skins are subjected in the course of their manufacture into leather.

A tanner should know something of the world-wide sources and availability of hides, skins and the various other materials necessary for leather manufacture and the government regulations pertaining to imports. It is important to be familiar with the types of damage to which hides and skins are liable, both on the living animal and after the slaughter. It is useful to know all the many operations involved in preparing hides and skins for delivery to the tannery and to be familiar with the hide market, the hide exchange and the principles of hedging.

It is essential for a tanner to understand the operations used in converting raw hides and skins into finished leather and the effect of each operation upon the properties of the finished leather. To be really successful, he must learn how to choose the raw stock best suited to make any given kind of leather, and how to regulate its characteristics by appropriate adjustments of the chemical and mechanical work done on it.

The value of leather in service lies only in its properties, and what the tanner has to sell is essentially only the properties of his leather. He should, therefore, learn to know his leather by its properties and to offer it only in terms of the suitability of its properties for any service that it must render.

Of all these things that a tanner should know, there is a minimum without which he might not be expected to continue indefinitely to operate success fully. As his knowledge grows beyond this minimum, he should be able to compete more and more successfully against tanners having less knowledge. The object of this book is to provide him with this minimum, in case he does not already possess it, and to indicate to him some of the simple ways in which he can increase his knowledge beyond it.

Although the operations of the tannery constitute a series of extremely complex chemical reactions and applications of physics equally complex, few practical tanners are versed in the fundamentals of either chemistry or physics. It thus becomes necessary to its widest field of usefulness that a book of this kind be written entirely in non-technical language. An attempt has been made to write this book in such manner that every portion of it can be read by anyone of average intelligence without the aid of a higher education.

Full use has been made of the writer's earlier volumes of "The Chemistry of Leather Manufacture" in selection of material of practical value, simplifying the language and bringing it up to date. This book also contains much new material that has never before appeared in print. In addition, such other material has been included from many sources as to make up the minimum that a tanner should know on all phases of the business of making leather. In following this plan, it has been the hope of the writer that the book will prove interesting and instructive to everyone with any curiosity about leather and animal skin.

A glossary of terms is included to explain the meaning of words belonging peculiarly to the leather and allied industries, trade names of materials, and scientific terms. It has not been considered practical to attempt to list the names of manufacturers of materials purchased by the leather industry, although the names of some manufacturers are given in parentheses after references to their products in detailed procedures. The publishers of this book also publish the "Chemical Engineering Catalog"; if it is desired to learn the sources of any of the many materials referred to in this book, the reader is referred to the "Chemical Engineering Catalog," which deals primarily with the sources of all commercial materials and engineering equipment and has the advantage of being brought up to date each year. Much valuable information on sources of materials and equipment can also be found in the Shoe & Leather Reporter Annual (Boston) and in Hide & Leather's Blue Book (Chicago).

The writer would not have presumed to write such a book as this without seeking the assistance of able men of the leather and allied industries. Special ists provided the details of many valuable procedures, tanners supplied photo

rials supplied detailed information on the properties and uses of their products. The Tanners' Council of America made available results of its surveys and researches, government bureaus supplied their latest statistics and regulations, and market men supplied information on hide prices and on the operations of the hide futures markets. It has been possible to acknowledge some of the assistance given in various parts of the text and under the photographs supplied. Since hundreds contributed to the making of this book, the writer has listed them below without regard to the nature of their contributions.

For assistance in the preparation of the manuscript, the writer is indebted to George D. McLaughlin, who read each chapter and offered many valuable suggestions; and to T. Blackadder, H. G. Turley, H. B. Walker and Henry Dietrich for reviewing and contributing to chapters on subjects in which they are expert.

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To the above and to any other contributors whose names may unintentionally have been omitted from the list, the writer expresses his thanks and assigns to them credit for whatever measure of success the book may have.

J. A. W.

11 West 42nd Street, New York, N. Y., December 11, 1940.

Contents

	Page
Preface	5
CHAPTER 1. HIDES AND SKINS AND THEIR HISTOLOGY	15
Classification and Nomenclature of Hides and Skins-Histology of Animal Hide-Cow Hide-Cell Reproduction-Epidermis-Hair-Thermostat Layer-Glands and the Thermostat Mechanism-Growth of Hide Fibers-Reticular Layer-Fibroblasts-Adipose Tissue-Blood Vessels-Elastin-Seasonal Differences-Nerves-Hyaline Layer and Sheaths-Reticulin-Grain Surface-Horizontal Sections of Cow Hide-Calf Skin-Flesh-Variations Over Skin Area-Sheep Skin-Goat Skin-Hybrids-Horse Hide-Hog Skin-Grain Patterns-References.	
CHAPTER 2. PREPARING HIDES FOR THE MARKET	59
Slaughter—Flaying—Curing—Building a Hide Pack—The Back Edge—Side Edges—The Spreads—Curing Action—Shrinkage—Effect of Delaying—Curing—South American Hides—Pickling—Drying—Salting and Drying—Bundling Hides and Skins for Shipment—Dried Stock—Pickled and Green, Salted Skins—References.	
CHAPTER 3. DOMESTIC PRODUCTION AND IMPORTS OF HIDES AND SKINS	75
Movement into Sight-Cattle Hides-Kip and Calf Skins-Sheep and Lamb Skins-Goat and Kid Skins-Imports for Consumption-Cattle Hides-Cattle Kips-Calf Skins-Goat and Kid Skins-Sheep and Lamb Skins-Dry Slats-Dry, Green and Wooled Skins-Pickled Skins, Fleshers and Skivers-Buffalo Hides-Indian Buffalo Hides-Horse, Colt and Ass Hides-Deer and Elk Skins-Reptile Skins-Kangaroo and Wallaby Skins-Shark Skins-Other Fish Skins-Seal Skins-Other Hides and Skins.	
CHAPTER 4. GOVERNMENT REGULATIONS ON IMPORTED HIDES AND SKINS	80
Tariff Act of 1930—Dutiable List—Free List—Changes in Import Duties and Trade Agreements—Dutiable List—Free List—Sanitary Control—Regulations of Bureau of Animal Industry—Restricted Countries—Methods of Disinfection of Restricted-import Hides and Skins—References.	
Chapter 5. Hide Damages	108
Damages Occurring on Living Animals—Mechanical Damages—Scratches—Wire Damages—Brands—Damages by Parasites and Diseases—Grubs—Lice—Ticks—Fleas—Mange—Scabies—Stephanofilariasis—Pox—Ringworm Scars—Warts—Damages Occurring After Killing—Flaying Damages—Butcher Cuts—Poor Pattern—Grain Cracks—Curing Damages—Salt Stains—Bacterial and Putrefactive Damages—Shipping Damages—Scratches and Abrasions—Wetting—Overheating—Localized Drying—Contamination—Guarding Against Losses—References.	
CHAPTER 6. PURCHASING HIDES AND SKINS	132
The Producer—The Collector—The Broker—Hide Prices—Speculation—Avoiding Speculation by Buying Hides When Selling the Leather—Avoiding Speculation by Contract Tanning—Avoiding Speculation by Hedging—	

Page

Spot and Futures Trading-Commodity Exchange, Inc.-Hide By-laws -Hide Trade Committees-Quotations for Hides-Grading and Warehousing Hides-Inspector-in-chief for Hides-Certification of Hides-Recertification of Hides-Appeal from Determination of Hide-Inspection Bureau-Inspection, Grading and Weighing of Hides-Validated Notice on Delayed Certification or Recertification-Charges for Certification of Hides-Provisions in Respect to Hide Certificates-Exchange of Hide Certificates-Limitations on Delivery of Certificates against New and Old Contracts-Cancelled Hide Certificates-Lost Hide Certificates-Storage and Transfer of Certificated Hides-Licensed Warehouses for Hides-Warehouse Receipts for Hides-Licensed Weighmasters for Hides-Delivery Points for Hides-Definitions and Construction in Respect to Hides -Extension of Credits for Hides-Commissions, Floor Brokerage and Charges on Hide Contracts-Hide Contract for Future Delivery-Tenderable Grades of Hides-Specifications for Deliverable Hides-Basis Grade-Contract Unit-Differentials-Adjustment for Seasonal Period of Take-off-Discounts for Special Factors-Special Factors Relating to Deliveries and Invoicing of Hides-Changes in Standards Affecting Grades and Selections of Hides-Hide Rules-Hours for Trading in Hides-Call for Hides-Delivery Months for Trading in Hides-Price Multiples for Hides-Price Fluctuation Limitation for Hides-Placing Hides in Deliverable Condition-Delivery and Payment for Hides-Hides Damaged by Fire, Smoke, Water or Other Causes—Title to Hides—Transferable Notice for Hides—Return Commission for Obtaining Business Unguaranteed and Guaranteed Accounts—The Tanner and the Hide Exchange-Effect of Speculation on the Hide Market Avoiding the Gamble of Hide-price Fluctuations While Making an Assured Profit on the Sale of Hide Futures-Avoiding the Gamble-Making the Profit—The Tanner as a Seller of Hide Futures-Selection of Hides for Specific Types of Leather-References.

CHAPTER 7. HANDLING RAW STOCK AS RECEIVED AT THE TANNERY

170

The Hide House—Trimming—Soaking—Soaking Green, Salted Calf-skins—Fleshing—Water—Bacteria—Antiseptics—pH Value—The pH Scale—Origin of Name—Colorimetric Measurement of pH Value—Soaking Dry Goatskins—Soaking Green, Salted Heavy Hides—Soaking Dry, Heavy Hides—References.

CHAPTER 8. UNHAIRING

201

Microscopic Study of Action of Limewater on Calfskin - Effect of Time and Temperature on the Hydrolysis of Skin and Hair by Saturated Limewater—Sulfides—Liming and Unhairing Green, Salted Calfskins—Scudding Calfskins—Washing and Cheeking—Other Sharpening Agents in Liming—Arsenic—Dimethylamine—Sodium Cyanide—Liming Goatskins—Liming Heavy Hides—Liming Hides for Sole Leather—Warm-water Pool—Enzyme Unhairing—Unhairing by Dissolving the Hair Dewooling Sheepskins—Sweating—By-products—References.

CHAPTER 9. BATING

237

Historical Development—Deliming and Bating Calfskins—Mechanism of Bating—Removal of Degradation Products of Epidermal System—Hydrolysis of Elastin Fibers—Hydrolysis of Collagen Fibers—Falling—Regulation of pH Value—Deliming—Bacterial Action—Bating Goatskins—Bating Sheepskins—Bating Hogskins—Bating Various Other Types of Stock—Bating Steer Hides for Sole Leather—Bating for Yards of Lower pH Value—Bating for Yards of Higher pH Value—Pickling—Drenching—References.

Page 272

CHAPTER 10. VEGETABLE-TANNING MATERIALS AND THEIR PROPERTIES

Commercial Sources of the Tannins—American Survey—Quebracho—Chestnut Wood—Mangrove Bark—Myrobalans—Wattle Bark—Valonia—Spruce Extract—Oak Bark—Hemlock Bark—Gambier—Sumac—Dividivi—Leaching Raw Tanning Materials—Use of Barkometer—Bisulfiting—Electrometric Measurement of pH Value—The Determination of Tannin—Cost of Unit of True Tannin—Relative Stability of Tanning Extracts Relative Fixation Values of Tanning Materials—Effect of pH Value on Color of the Tannins—Effect of pH Value on the Oxidation of the Tannins—Effect of pH Value on the Precipitation of Quebracho Liquors—Acid Fermentation in Tan Liquors—Discoloration of Tannins by Iron—References.

CHAPTER 11. VEGETABLE TANNING

306

Vegetable-tanning Bated Calfskins—Vegetable-tanning Pickled Calfskins—Vegetable-tanning Sheepskins—Vegetable-tanning Hogskins—Vegetable-tanning Gole Leather—Rocker Yard—Layer Yard—The Leach House—Rapid Tanning of Sole Leather—Vegetable-tanning of Pickled Steer Hides—Vegetable-tanning Horse Hides—Vegetable-tanning Harness and Strap Leather—Vegetable-tanning Heavy Strap Leathers of Great Strength—Vegetable-tanning Miscellaneous Leathers—Diffusion of Tannin into Hides—Distribution of Tannin Through Thickness of Leather—Effect of Time and Concentration of Tan Liquor upon Tannin Fixation—Effect of pH Value on Fixation of Tannin—Effect of Kind of Acid on Tannin Fixation—Effect of Neutral Salts on Tannin Fixation—Effect of pH Value and Added Salt on the Plumping of Stock in Tan Liquors—Effect of Temperature on Tannin Fixation—References.

CHAPTER 12. CHROME TANNING

363

Making One-bath Chrome Liquors—Chrome-tanning Pickled Caliskins—Determination of Hide-substance Content of Pickled Stock Before Chrome Tanning—Chrome-tanning Pickled Cowhides—Chrome-tanning Goatskins by Two-bath Process—Chrome-tanning Sheepskins by One-bath Process—Chrome-tanning Sole Leather—Chrome-tanning Horschides—Chrome-tanning Shearlings—Commercial One-bath Chrome-tanning Materials—Chrome-tanning for White Leathers—Chrome-tanning Cowhides for White Leathers—Chrome-tanning Goatskins for White Leathers—Chrome-tanning Sheepskin Skivers for White Leathers—Effect of Adding Salts of Organic Acids on Chrome Tanning—Tanning Calfskins with Chrome-formate Liquor—Materials Used in the Construction of Drums and Paddle Vats—General Properties of One-bath Chrome Liquors—Effect of Concentration of Chrome Liquor on Its pH Value—Effect of Adding Neutral Salts to a Chrome Liquor on Its pH Value—Effect of Concentration of Chrome Liquor on Fixation of Chrome by Hide Substance—Effect of Added Salts on Chrome Tanning—Effect of Time and Temperature on Chrome Tanning—References.

CHAPTER 13. MISCELLANEOUS TANNAGES

412

Chrome Retanning—Syntans—Alum Tanning—Aldehyde Tanning—Calgon Tanning—Calgon-vegetable Tanning—Calgon White Leathers—Calgon-chrome Tannages—Oil Tanning—Tungsten Tanning—Quinone Tanning—Miscellaneous Tannages—References.

Page

CHAPTER 14. LIGHT LEATHERS FROM TANNING TO FATLIQUORING AND MOLD CONTROL

438

Pressing—Wringing—Setting Out—Splitting—Shaving—Assorting—Washing and Neutralizing Chrome-tanned Stock—Bleaching and Retanning Vegetable-tanned Calfskins—Permanganate Bleach—Mold Growths—Preparation of Cultures for Study—Nature of Growth—Industrial Importance—Other Molds—Prevention of Mold Growths—References.

CHAPTER 15. FATLIOUORING, STUFFING AND DYEING LIGHT LEATHERS

468

Fatliquoring Vegetable-tanned Light Leathers—Fatliquoring and Dyeing Black Chrome-tanned Leathers for Dress-shoe Uppers—Patliquoring and Dyeing Colored Chrome-tanned Leathers for Dress-shoe Uppers—Dyeing Vegetable-tanned Leathers for Shoe Uppers—Dyeing and Fatliquoring Stock Chrome-tanned in Presence of Sodium Formate—Elk Leathers—Dyeing and Stuffing Waterproof Chrome-retanned Upper Leathers—Dyeing and Fatliquoring Chrome-tanned Goatskins—Dyeing and Fatliquoring Chrome-tanned Sheepskins—Dyeing and Fatliquoring Heavy Glove Leathers—Coloring Suède Leathers—Dyeing and Finishing Aniline Bag and Case Leathers—Fatliquoring Prootball Leathers fatliquoring White Leathers—Oiling and Dyeing Shearings—Pats and Oils Used in Fatliquoring and Stuffing—Spews—Gummy Spews—Soaps—What Fatliquoring Does to Leather—Effect of Depth of Penetration of Oils into Leather—Sulfonated Oils—Egg Yolk—Phosphorated Oils Moellon Degras—Mineral Oils—Stuffing Greases—Colloidal Clays—Aniline Dyestuffs—Natural Dvestuffs—References.

CHAPTER 16. DRYING LIGHT LEATHERS AND MECHANICAL OPERATIONS

518

Drying Vegetable-tanned Calf Leathers—Drying Chrome-tanned Calf Leathers—Dampening Chrome-tanned Leather for Staking Staking Tacking or Toggling—Knee Staker—Air Conditioning—Solubility of Water in Air—Relative Humidity—Relative Humidity—Tables How to Use the Tables—The Anemoneter—An Innovation in Preparing Leather for Staking—Pasting—Drying Equipment—Buffing—Buck Leathers—Suède Leathers—Wetting Agents—Other Types of Buffing Machines—Brushing—References.

CHAPTER 17. FINISHING LIGHT LEATHER

556

Simple Finishes for Chrome-tanned Calf Leathers Finishing Black Chrome-tanned Calf Leather—Glazing Plating Finishing Colored Chrome-tanned Calf Leather—The Break of Leather Aniline Leathers and Pigment Leathers—Simple Finishes for Vegetable-tanned Calf Leathers—Finishing Black Vegetable-tanned Calf Leathers—Finishing Black Vegetable-tanned Calf Leathers—Finishing Colored Vegetable-tanned Calf Leathers—Boarding or Graining Troning—Embossing—Building a Matrix for Embossing on a Sheridan Press—Embossing—Building a Matrix for Embossing on a Sheridan Press—Embossing—Plates—Smoothplating—Assorting and Grading—Leathers—Measuring Areas of Calfskins—Checking and Bundling—Raw Materials—Used in Leather—Finishes—Protein Materials—Gums and Mucilages—Natural Resins—Waxes—Pigments—Dyes—Antiseptics—Rubber Latex—Pyroxylins and Synthetic Resins—Miscellaneous Materials—Finishing Miscellaneous Leathers—White Leathers—White Elk Side Leather—White Sheep Pouch Bag—Leather—Glazed Kid—Leather—Lining Kid—Leather—Crushed Kid—Leather—Sheepskin Garment Leather—Lining Leather—Clase—Leather—Hat Sweatband—Leather—Unglazed Wax—Enamel Leather—Colored—Side—Leather—Gun—netal—Side—Leather—Water-lacquered—Leathers—Elk Side—Leather—Lining—Splits—Horsehide Garment Leather—Case—Leather—Black Vegetable-tanned—Strap and Portfolio—Leathers—Buse—ball—Leather—Two-tone—Basketball—Leather—Golf-grip—Leather—Saddle

729

CONTENTS

Leather—Gold and Silver Leathers—Patent Leathers—The First Coat—The Second Coat—The Third Coat—Sunning—Lacquering—Photomicrographs—References.	Page
CHAPTER 18. SOLE AND HEAVY LEATHERS	614
Cropping—Extracting—Tempering—Bleaching—The Oil Wheel—Drying —The Sour Dip—Sponging and Rolling—Finishing—Finders' Bends—The Dry Dip—Chrome Sole Leather—Harness Leather—Fatliquoring—Stuffing —Buffing—Blacking—Waterproofing—Miscellaneous Leather—Water- proofing Sole Leather—References.	
CHAPTER 19. THE PROPERTIES OF LEATHER	629
Physical Structure—Chemical Composition—Strength and Stretch—Effect of Splitting—Effect of Relative Humidity—Effect of Oil Content—Effect of Kind of Tannage and Method of Finishing—Strength, Stretch and Tearing Resistance of Various Satisfactory Leathers—Ventilating Properties of Leather—Permeability to Water Vapor—Effect of Temperature—Effect of Relative Humidity—Relative Porosity—Effect of Oil Content—Effect of Finishing—Directional Effects—Ventilating Properties of Various Leathers—Dimensional Changes in Leather with Relative Humidity—Effect of Time—Effect of Glycerin—Practical Tests—Temper of Leather—Effect of Splitting—Typical Temper Values—Resilience of Leather—Resilience of Typical Leathers—Effect of Water and Grease—Wear Resistance of Leather—Firmness of Heavy Leathers—Resistance of the Grain of Leather to Cracking—Resistance of Leather to Hot Water—Effect upon Lasting in Shoe Making—Ability of Leather to Retain Embossing—The Break of Leather—Color and Warmth—Resistance of Leathers—Effect of Concentration of Acid—Action of Hydrochloric Acid—Effect of Relative Humidity—References.	
GLOSSARY	705
NAME INDEX	725

SUBJECT INDEX

Chapter 1

Hides and Skins and Their Histology

Leather is animal hide or skin so treated chemically as to make it permanently more resistant to decomposition, particularly when wet. Any animal hide or skin may be converted into leather, but many are not used commercially for this purpose because of their small size, scarcity or lack of demand for the kind of leather they would make.

Most leather is made from the hides or skins of animals slaughtered for food, and practically all such hides and skins removed from meat-producing animals are converted into leather, regardless of the demand for leather. The demand for meat and not the demand for leather determines the production of leather. An increasing demand for leather merely increases the dollar value of both hides and leather. When the demand for leather falls off, production of leather may decrease temporarily, but the accumulations of hides at decreasing money value quickly restore the production of leather to keep pace with the slaughter. For example, following the devastating effects of the World War, the demand for leather in 1919 increased the value of domestic cattle hides to about 70c per pound, but the falling off in demand in 1932 lowered the price below 4c. The dollar volume of leather production varies widely over the years, but the actual quantity volume simply follows the slaughter caused by the demand for meat. Leather is really a by-product of the meat industry.

This adds an annoying element of speculation to an industry already highly competitive, making it essential to survival for leather manufacturers to learn the principles of "hedging"; to keep alert to the fundamental, world-wide factors that directly or indirectly influence hide prices; to keep informed of the ever-increasing scientific knowledge relating to the more efficient manufacture of leather; and so to control the properties of their products as to meet the changing demands of a growing civilization.

As removed from an animal, a hide is covered with bacteria, and is readily putrescible; much more than one-half of its weight consists of water. Bacterial action is greatly retarded by common salt. In the domestic production of cattle hides, it has become customary to preserve them by packing them in salt, which dissolves in the water of the hide, protecting it from the putrefactive action of bacteria. This process, known as curing, will be described more fully in Chapter 2. Although some of the water of the hide is lost during curing, most of it remains. Before curing, the hide is referred to as being in the green state. After curing, it is said to be in the green, salted state. This is mentioned here because the given weight of a hide usually refers to its weight in the green, salted state. Hides are sometimes preserved by drying, which causes a loss of more than 50 per cent in weight simply because of the loss of water; but they are often classified according to the weight they would have had in the green, salted state, if they had been cured like most domestic cattle hides, although in an actual sale or for import records the dry weight is used for dry hides.

4 -

Classification and Nomenclature of Hides and Skins

A skin is simply a small hide. In the case of cattle, a hide weighing less than 15 lbs. in the green, salted state is called a calf skin. When it weighs from 15 to 25 lbs., it is called a kip. When it weighs from 25 to 30 lbs., it is called an overweight kip. When it weighs more than 30 lbs., it is called a hide. A cow hide weighing less than 53 lbs. is called a light cow and one weighing more than 53 lbs. a heavy cow.

Hides from male animals are classified as bull, steer and stag according to characteristics of the hides caused by castration. Bull hides are from animals that have not been castrated, and are characterized by very thick and rough head, neck and shoulders and loose flanks. As a rule, bull hides are not only poor in quality, but heavy in weight, ranging from about 60 lbs. each to more than 100 lbs. Fortunately, they constitute only about 4 per cent of total production.

Steer hides are from animals castrated as calves, often at the age of about three months. The effect of castration is a much more satisfactory development of the hide as well as of the meat. The hide becomes much smoother and more uniform in thickness and structure, as well as much denser and tighter than that of a bull. Steer hides are used to make the best grades of sole leather and are to be preferred to cow hides, which have a looser structure. In very young calves, the skin of the female produces a finer piece of calf leather than that of the male; and this difference apparently persists throughout the lives of the animals, except for the marked effects of castration, which cause the hide of the steer to become far superior to that of the cow. A cow hide is superior to a bull hide, although lighter in weight.

Stag hides are from male animals not castrated at so early an age as the steers, often not until they are over a year old. During the period preceding castration, they develop hides like bulls, and the longer castration is delayed, the more like bulls they become. In the hide market, stag hides have no official designation of their own and are accepted as steers or bulls, whichever they more nearly resemble. This is often annoying because they mask that sharp line of differentiation between steers and bulls.

A steer hide weighing less than 48 lbs. is called an *ex-light steer*. When it weighs from 48 to 58 lbs., it is called a *light steer* and one weighing more than 58 lbs. is called a *heavy steer*.

As in many of the ancient arts, the leather industry has a language of its own and uses many terms in common use, but with very different meanings from those in common use by the layman. For this reason, the reader is cautioned to familiar ize himself with the definitions given in the Glossary at the end of this book, which includes some scientific terms as well as many belonging peculiarly to the leather industry. For example, *chamois leather* is not usually made from the skin of the mountain antelope of Europe and Asia bearing that name, but from the reticular layer of domestic sheep skins. *Elk leather* is usually made from cow hide, and the name refers merely to the methods used in tanning and finishing. *Kid leathers* are usually made from the skins of mature goats. *Russia* calf leather is made in the United States, and is so named because it is vegetable tanned and scented with birch oil, resembling a leather once made in Russia that was tanned with extract from the bark of the Russian birch tree.

A native cow hide is one from an animal that has not been branded, the term native merely indicating that the hide is free from brand marks. A Colorado steer hide may never have been near the state of Colorado; the term merely means that the hide has been branded on the side or butt area, or both. If a hide of this

description is of compact, narrow and close pattern and plump, it is a *Texas* steer hide. If a steer hide is branded on the butt area back of the break in the flank, it is known as a *butt-branded* steer hide. If the animal was slaughtered and flayed in one of the packing plants known in the trade as West Coast plants, the hide is known as a *Pacific Coast* hide.

Hides that are unusually wide are often called *spready*, and their surface areas are often large in proportion to their weights. *Plump* hides have a dense and uniform structure and usually have surface areas small in proportion to their weights. In cold weather, animals usually have longer hair and their hides lose less water in curing and bundling than those of animals slaughtered in hot weather. The skins of calves less than two months old are structurally not the same in cold and in hot weather, an important point that will be treated more fully later in this chapter. Hides are designated according to the time of year that the animal was slaughtered as *January hides*, *June hides*, *October hides*, etc. or sometimes merely as winter hides or summer hides. It is important for the tanner to know which he is buying, because it greatly affects the yield and quality of leather he gets from them. Hides taken off during the months of July, August and September usually give him the best results. A winter hide contains less hide substance and more hair weight than a summer hide.

For light suede leathers, fine pocketbook leathers, drumheads, parchment, etc., the skins of unborn or prematurely born calves are often found most desirable. These skins are referred to as *slunks*.

In the largest packing plants, many butchers assist in *flaying*, or removing the hide from a single animal. Each of these butchers becomes highly skilled in one portion of the work of flaying, which will be described detail in Chapter 2. This high degree of specialization results in less damage due to improper flaying, and the subsequent curing is also carried out more efficiently in the largest plants, resulting in a superior hide for manufacture into leather. Such hides are referred to as big-packer hides. In the smaller packing plants, where there is less specialization, the hides are usually of a lower standard, and are known as small-packer hides. Hides taken off by city butchers are known as New York City butchers, Milwaukee butchers, etc., and tanners usually learn by experience which are most suitable for their purpose and economical to buy. Most hides taken off by country butchers and inexperienced farmers are badly damaged in flaying and are not well cured, although they may have come from animals of the same class as those of the big-packer hides. Such hides are referred to as country hides.

Hides from many foreign countries are preserved merely by drying and are known as dry hides or flint hides. Others are treated with salt and then dried, and are known as dry, salted hides. Hides cured with salt, but not dried are known as green, salted hides. In various countries, hides of the same type differ greatly in suitability for certain types of leather because of feeding, climatic conditions, heredity, methods of flaying and of preservation, etc. Argentina has a great packing industry and exports much frozen beef. The hides are well flayed and cured and come to this country in the green, salted state. Those corresponding in quality to our big-packer hides are known as Prigorifico hides; those more like our small-packer hides as Saladero hides and those corresponding to our country hides as Matadero hides.

Out of a total of more than 19 million cattle hides made available to American tanners in 1939, more than 16 million were of domestic production and less than 3 million were imported. More than 11 million kip and calf skins were of domestic production and less than 4 million were imported. Practically all the more than

39 million goat and kid skins made available to American tanners in 1939 were imported; nearly 38 million were received in the dry state and a little over one million in the green, salted state. Of the total of about 47 million sheep and lamb skins, about 42 per cent represented domestic production and about 58 per cent was imported. Production and imports are discussed more fully in Chapter 3.

Goatskins are usually named after the country or province of origin, such as Amritsars, Brazilians, Capetowns, Chinas, Mochas, Moroccos, Pernambucos, Turkestans, etc. Although most of them arrive in the dry state or dry, salted state, they vary greatly in quality and suitability for different types of leathers.

Most of the packer sheep skins are dewooled at the packing plant, then preserved by *pickling* with a solution of sulfuric acid and salt, and sold as *pickled sheepskins*. Although most of the imported sheepskins arrive in the *pickled* state, many are *dry*, or *dry*, *salted* and some are not dewooled. The domestic skins from the big packers usually carry the name of the packer and imported skins take the name of the place of origin.

For making cheap shoe and other leathers, American tanners sometimes buy *East India kips*, which are from fully grown buffalos, but called kips because of their size. They are received already unhaired and at least partially tanned. The tanner retans them and finishes them according to the type of leather desired. Mr. C. A. Andres, 87 Gold Street, New York City, has given the writer the following information about the industry in British India.

"The tanning of hides and skins in British India is a considerable industry and lies in the hands of hundreds of small tanners. The main export center is Madra; in southern India, but tanned hides and skins are also exported through the port of Bombay. The Bombay tannages in goat and sheep are of lower value than the Madras tannages, but the tanned cow hides and buffalos bring about the same price as the Madras tanned hides. The texture of the hides and skins exported through Bombay is not as tight and firm as those exported through Madras. A small amount of tanned hides and skins is exported from Karachi, but those tannages are very inferior.

"The United States imports only a small percentage of the tanned goat skins and sheep skins produced in India, but at times considerable quantities of tanned cow hides and buffalo hides are imported by this country. That depends entirely upon the relative positions of the American and Indian hide markets. The main use for India tanned hides in the United States is for cheap shoe leather. A lesser amount is used in the production of bag and fancy leathers. East India tanned goat and sheep skins were at one time used largely in the production of shoe leather, but in late years have been principally used for fancy leather.

"The India tannage is a tannage peculiar to India and cannot be duplicated elsewhere. If a tanner in the United States or in Europe were to buy the same raw hide as the tanners in India do, he could not produce the India tannage. That may sound funny, but it is so. A characteristic of the India tanned hide and skin is its good tensile strength."

In the United States horse meat is not a popular food and so most of the domestic hides are from horses that have died in service or met with accident. The flaying and curing are often done long after the death of the animal and rarely, if ever, with the great efficiency associated with packer cattle hides. Much of the domestic stock is thus of relatively low quality. Most of the green, salted horse hides are obtained from France, Argentina, Canada, United Kingdom, Belgium and Netherlands, decreasing in volume in the order given. Most of the dry horse hides are obtained from Argentina, but some are obtained from France and Canada.

The horse hide is peculiar in having extraordinarily dense fibrous structures in the butt areas, from which cordovan leathers are made; the rest of the hide has an unusually loose structure, making it more suitable for baseball, garment, glove and other types of leathers. Some tanners require only the butts and others only the looser areas. For this reason some dealers cut the hides into horse butts and horse fronts and sell them separately.

In the United States, packers leave the skin of hogs on the meat and have to offer only strips of skin over the lard areas. These strips often measure only about 24x6 inches, but find a place in the manufacture of leather for shoc counters. As most of the country skins made available are of low quality, the best hog skins have to be imported. Kangaroo and wallaby skins come only from Australia and are received as dry skins. In Chapter 3, tables are given showing the imports of all kinds of hides and skins for the calendar year 1939 as well as such figures on domestic production as could be obtained.

Since animal hides and skins constitute the one fundamental material from which all leather is made, it is of tremendous importance to success for a tanner to be intimately acquainted with their structure, composition and functions and their variations in different animals and in different parts of the same animal. The branch of biology that deals with the minute structure of animal hides and skins is known as histology, or microscopic anatomy. The rest of this chapter deals with this topic.

Histology of Animal Hide

The structure of animal hides can best be studied by cutting very thin cross-sections, mounting them on slides and observing them under a powerful microscope. The sections can then be photographed at very high magnifications for more convenient study. The methods of preparing such sections and photographing them are described in minute detail in the author's *The Chemistry of Leather Manufacture*, Vol. II, Chapter 36, pages 967 to 1028; this book contains also about 150 photomicrographs of hides and skins and of leather that are worthy of detailed study by all interested in leather and its manufacture. Some of these are reproduced in this book for convenience, together with many new ones which were not available when the earlier book was published.

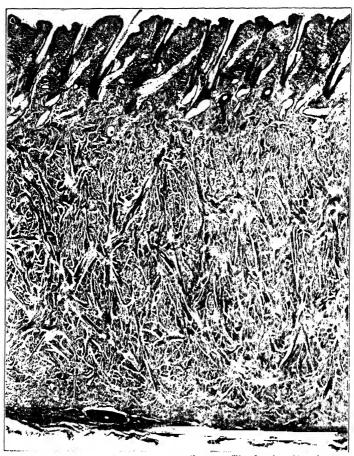
Cow Hide

Fig. 1 shows a thin slice, or cross-section, cut from the butt area of a fresh cow hide, photographed through a microscope at a magnification of 16 diameters. It is customary to refer to magnifications in photomicrography in terms of diameters, which means the number of times that one dimension has been increased in length. Since the hide has three dimensions, it would have to be 16x16x16, or 4096 times its actual size or volume for its cross-section to appear as it does in Fig. 1.

This section is known as a *vertical* section because it was cut in a vertical direction with respect to a hide laid out flat in a horizontal plane. The hair side of the hide is seen at the top of the picture and the flesh side at the bottom.

All hides are divided sharply into three layers, distinct both in structure and origin: (1) a relatively very thin outer layer of *epithelial* tissue called the *epidermis*; (2) a very much thicker layer of *connective* and other tissues, called the true skin, *derma* or corium; and (3) a relatively thin layer called the *superficial fascia*, but known to the tanner simply as the *flesh* and containing *adipose* (fatty) and *arcolar* (loose connective) tissues and sometimes *muscle* tissues.

In Fig. 1, the *epidermis* appears as a thin, dark line covering the entire upper surface of the hide and constituting only about $\frac{1}{200}$ th of the total thickness of the hide. The *flesh* appears as the dark band covering the lower surface of the hide and constituting only about $\frac{1}{20}$ th of the total thickness of the hide. All of that portion between the epidermis and the flesh is the *derma*, or true skin.



Courtesy The Leather Manufacturer.

Fig. 1. Vertical Section of Cow Hide.

Location: butt.
Thickness of section: 20 microns, or 0.00079 inch.
Magnification: 16 diameters.

In biology, a tissue is defined as one of the elementary fabrics of which an organ is composed, formed by cells and/or their products arranged in a definite manner or pattern. A hide is composed of many tissues with which a tanner should be very familiar and they will be described individually. An organ is a part of the body that performs some definite function, and a hide is a vital organ of the body.

Cell Reproduction

The epidermis and hair consist chiefly of epithelial tissue, which is made up of living, self-reproducing cells covered with layers of dead cells which are gradually worn away, making room for the steady reproduction of new cells below. Epithelial cells cover all free surfaces on and in the animal body. Each individual, self-reproducing cell is a separate and distinct living organism, consisting of a nucleus suspended in protoplasm enclosed between very thin walls acting as semi-permeable membranes. The cell has no sex, but is capable of self-reproduction.

The first operation in the reproduction of cells is the diffusion of nourishment into a cell through the membranous walls. This is followed by a period of growth. In the protoplasm, besides the nucleus, there is a small, round, highly refractive body of protoplasm known as a centrosome, which separates during the period of growth into two centrosomes which then repel each other. The nucleus contains a protein body known as chromatin, which now separates into a number of unit segments called chromosomes, each of which splits longitudinally. One-half of each chromosome passes in the opposite direction toward a centrosome. In this manner each new daughter cell receives exactly the same number of structures as were found in the parent cell. The longitudinal halves then constitute the chromosomes of the daughter cells and gradually become mature structures, while the cell wall constricts, forming two new complete and separate cells.

Epidermis

As the epidermis has no blood vessels, the food required for the reproduction of the epithelial cells is drawn from the derma below. Fig. 2 shows the epidermis of the skin of a man's chin magnified 3500 diameters and thus made to appear as though the man were 42,875,000,000 times his actual size. At this tremendous magnification each individual cell and its contents can be seen very clearly. In order to get sharp definition in a picture at this magnification, it was necessary to cut the section of skin only woodth of an inch thick. This is less than one-half of the diameter of a single cell, and this must be taken into consideration in noting the honeycomb structure of the epidermis. It will be noted that tiny, fiber-like processes separate the individual cells; these are often called prickles. Extending between prickles there are protoplasmic processes, and it is supposed that food passes upward between the cells and the waste products downward. From this food, the cells derive the nourishment necessary for reproduction. This region contains no blood vessels, but very fine nerve fibers pass into it from the derma, forming a network between the cells and terminating in bulbous swellings or undergoing a gradual breaking up into nerve granules.

As the new cells are formed, the older ones are pushed outward to a point where there is a diminishing supply of nourishment; these cells die and their protoplasm gradually dries up. Near the top of the picture, two cells can be seen in the first stages of this drying. Above them the cells have flattened out, forming the flaky sheets that are gradually worn away and appear on the scalp as dandruff, which is not in itself a disease, but a perfectly normal casting off of dead epithelial tissue, which is a continuous process. The picture also shows cells in various stages of reproduction.

Hair

Fig. 3 shows a portion of the grain layer of Fig. 1 at a magnification of 75 diameters. It includes a hair in its follicle. The follicle is formed by an indentation



196, 2. Vertical Section of Epidermis of Human Skin.

Location: chin. Thickness of section: 5 microus, or 0.00020 inch. Magnification: 3500 diameters.

of the epidermis into the derma. The epithelial cells that cover the bottom of the follicle receive an abundance of nourishment from a projection from the derma into the follicle known as a hair papilla. The epithelial cells surrounding the papilla reproduce in large numbers and the older cells are pushed upward through the follicle forming the hair, which is really of the same composition as, and a part



Courtesy The Leather Manufacturer.

Fig. 3. Vertical Section of Thermostat Layer of Cow Hide,

Location: butt.

Thickness of section: 20 microns, or 0.00079 inch. Magnification: 75 diameters.

of, the epidermis. A hair papilla passing into the bulb of a hog hair is shown in Fig. 4. In the course of their travel up through the follicle, the epithelial cells adhere to one another strongly as they die and dry up, forming a tough hair, which takes its shape from that of the follicle. The formation of hair is a continuous operation so long as food for the epithelial cells remains available. If a hair is pulled out of a living animal, the reproducing cells in the follicle soon replace it.



Fig. 4. Vertical Section of Hog Skin Showing Hair Papilla Passing Into Hair Bulb

Location: butt. Thickness of section: 20 microns, or 0.00079 inch. Magnification: 225 diameters.

The hair papillae contain blood vessels which supply not only food, but also coloring matter of the blood to the reproducing cells; thus the hair grows with a color as long as the coloring matter is available. In a man's scalp, when the arteries of the hair papillae harden sufficiently, they will not pass the coloring matter of the blood; the epithelial cells then reproduce without coloring matter and the hair appears gray. When they harden to the point that they pass no blood at all, the man becomes bald.

The hair shaft above the outer surface of the skin consists of dead epithelial tissues. Stories of such hair turning gray over night because of shock or worry are sheer nonsense. Gray hair consists of epithelial cells which had no coloring matter from the blood at the time they were produced from their parent cells. The only cure for baldness would be a new system of blood vessels that would carry food to the living epithelial cells at the bottom of the follicles, and no one has yet discovered how to provide a new system for the purpose.

Thermostat Layer

Examining Fig. 1 closely, it will be observed that the derma itself is divided rather sharply into two layers: the top one-fifth of the thickness which contains the hair roots and the lower four-fifths, consisting chiefly of a fibrous structure. The upper layer is shown in Fig. 3 at greater magnification. The tanner calls it the *grain layer* because it forms what is known as the grain of the leather, but the writer has called it the *thermostat layer* because its function in the animal body is that of a thermostat.

If the body temperature of a man exceeds 98.6°F., he is said to be running a temperature or having a fever; if it exceeds 110°F., he usually dies. If it falls much below 90°F., he usually dies. To be in good health, the average man must maintain a body temperature within one degree of 98.6°F. The same principle holds true for practically all warm-blooded animals. Within the body so much heat is being developed continuously that the body temperature would be raised above the death point in the course of ten to fifteen minutes, if no means were provided to throw off this heat in amounts necessary to keep the body temperature constant. Death would result from either too rapid or too slow a loss of heat by the body. The skin is the vital organ of the body that controls its temperature.

Glands and the Thermostat Mechanism

Close to the bottom of the hair follicle shown in Fig. 3, there is attached an erector-pili muscle, which can be seen weaving its way upward to the right of the follicle. Just below the point of attachment of this muscle to the hair follicle can be seen an open space containing the sudoriferous or sweat glands. In the animal body, glands are composed of living cells which, according to their kind, separate and take from the blood the materials which they need for their own reproduction and then throw off as waste products materials that may be of vital importance to the whole body. Fig. 5 shows a cross-section of a sweat gland in a human scalp photographed at a magnification of 2330 diameters. The cells are bound together in a membranous sac with a duct leading to the outer surface of the skin. As the food required for their own reproduction, these cells selectively take various waste products from the blood, including protein decomposition products, salts and an abundance of water. Through the duct leading to the skin surface they excrete water, urea and salts together with the decomposition products of the excess cells produced; in fact, they serve the body as an excretory organ much as the kidneys do, but their vital task is to bring water to the skin surface.

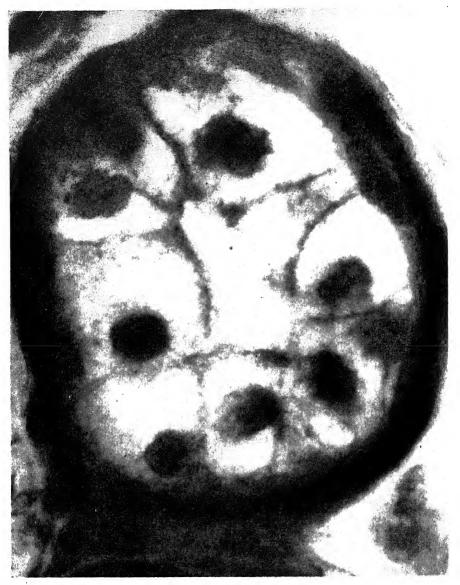


Fig. 5. Vertical Section of Sweat Gland of Human Skin.

Location: scalp.

Thickness of section: 10 microns, or 0.00039 inch. Magnification: 2330 diameters.

Water is a common material having a very high specific heat and also a very high latent heat of vaporization. The specific heat of a material is defined as the quantity of heat required to raise the temperature of one gram of the material 12C. The quantity of heat is usually expressed in calories. A calorie is the amount of heat required to raise the temperature of one gram of water by 1°C. Water freezes at 0°C, and boils at 100°C, and so it requires 100 calories to raise the temperature of one gram of water from the freezing point to the boiling point. The specific heat of water is taken as unity, or 1.00000 calorie, at 15°C, because it varies slightly with temperature; but the extreme deviation from unity from the freezing point to the boiling point of water is less than 1 per cent. The specific heat of most other materials is less than 1.0. For mercury it is only 0.0333.

The latent heat of vaporization of a liquid is defined as the number of calories required to change one gram of it to vapor without changing its temperature. The latent heat of vaporization of water decreases from 595.9 calories at the freezing point to 539.6 at the boiling point. Only 100 calories are required to raise the temperature of one gram of water from the freezing point to the boiling point, but nearly 540 calories are required then to vaporize it without further increase in temperature.

If water is kept in contact with an atmosphere that is not saturated with water vapor, it will evaporate, taking the required heat of vaporization from its surroundings. At body temperature, the evaporation of one gram of water will cause a loss of heat from its surroundings of about 574 calories. The flow of water from the sweat glands to the skin surface and its subsequent evaporation is continuous, just as the development of heat within the body is continuous.

It is essential to the life of the body that the excess heat continuously developed be exactly balanced by the heat losses so that constant body temperature is maintained. The rate of evaporation of water at the skin surface must be controlled. In the $\mathcal V$ formed by the erector-pili muscle and the hair follicle shown in Fig. 3, there can be seen the sebaceous glands which appear to rest on the muscle and open into the follicle.

Fig. 6 shows a cross-section of a sebaceous gland in the skin of a human chin photographed at a magnification of 3500 diameters. The cells are bound together in a membranous sac with a duct opening into the hair follicle at a point about one-third of the distance from the bottom of the follicle to the top. As the food required for their reproduction, these cells selectively take carbohydrates and other materials from the blood, which are converted into oils and waxes in the course of the reproduction and stored within the cell walls, where they can be seen rather plainly in the picture.

Although they cannot be seen very readily from Fig. 3, there are tiny pilomotor nerves extending from the epidermis to the erector-pili muscle. These nerves are very sensitive to temperature changes. When the temperature at the skin surface drops too much, these nerves activate the erector-pili muscle, causing it to contract. The goose-pimples commonly seen on the skin when exposed to cold air result from the contractions of these nuscles, which cause a rupture of many of the cells of the sebaceous glands, and their oily contents are exuded into the hair follicles. The phenomenon of oil spreading over watery surfaces is a sight familiar to almost everyone. The oil liberated into the hair follicle immediately starts spreading over the wet surface of the skin and, in so doing, decreases the rate of evaporation of water from the skin surface. This continues until the heat balance of the body is again restored. The pilo-motor nerves so control the activity of the erector-pili muscles that the proportion of oil to water liberated by the glands is just what is required to maintain body temperature.

Like practically all forms of life, the cells of the sebaceous glands work primarily for their own reproduction and preservation and not for that of the entire body, which must have its own system for making use of its glands. If the body



Fig. 6. Vertical Section of Sebaceous Gland of Human Skin,

Location: chin. Thickness of section: 10 microns, or 0.00039 inch. Magnification: 3500 diameters.

HIDES AND SKINS AND THEYR & ISTOLOGY



Fig. 7. Vertical Section of Single Hide Fiber in Cow Hide.

Location: butt.

Thickness of section: 30 microns, or 0.00118 inch.

Magnification: 1625 diameters.

needs oil at the skin surface, it sacrifices the lives of cells of the glands until the needs are met. On the other hand, the cells reproduce according to the supply of food available to them rather than according to the needs of the body as a whole. A too rich diet when the oils are not needed may result in an overproduction of the cells, which will not be destroyed by the muscles unless oil is required. The result

is boils, pimples and blackheads which readily become infected. If the muscles become sluggish through lack of exercise, they may not be ready to respond quickly enough to a sudden chilling of the body and the resulting upset may give bacteria an advantage in the body that will result in colds, pneumonia or other diseases.

Growth of Hide Fibers

Referring again to Fig. 1, it will be noted that the derma, which is the portion of the hide made into leather, consists chiefly of interlacing fibers. Below the thermostat layer they are relatively large and constitute the bulk of the hide. These fibers are composed of a protein substance called *collagen*, which means "glue forming." Most tanners know that glue can be made by treating hide scrap with boiling water. The resistance of the hide fibers to boiling water increases with the age of the animal, requiring more prolonged boiling to get it into solution. The more drastic treatment causes greater decomposition of the protein. For this reason scraps of calf skin are used in the manufacture of good grades of edible gelatin and the older hides are used to make glue. We have learned much about collagen by experimenting with the purest grades of gelatin in order to eliminate the disturbances caused by the complex anatomical structure of the hide.

The epidermis, hair and glands are composed of reproducing cells so that the older tissues are continually being replaced by new ones. This is not true for the collagen fibers because they are not made up of cells and do not reproduce themselves. Collagen is a protein secreted by certain white corpuscles of the blood known as fibroblasts, each of which consists of a single cell. During the period of growth of an animal, fibroblasts leave the blood streams and migrate outward through the skin, each one exuding collagen material along the path of its travel, the exuded material becoming a single, long fibril. The fibroblast may thus be likened in its action to a silk worm that spins out a long filament or fibril of silk in forming its cocoon. During the period of growth of the animal, each fiber increases in size by the repeated addition of fibrils by the migrating fibroblasts. A single hide fiber is thus made up of many fibrils.

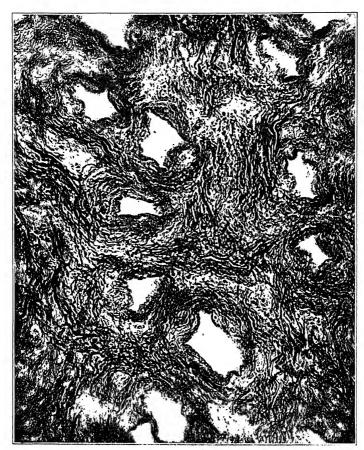
Fig. 7 shows a cross-section of a single fiber in a cow hide magnified 1625 diameters. The fiber appears somewhat elliptical in shape with a major axis of a length of 0.0034 inch and a minor axis of 0.0020 inch. The cross sections of the fibrils appear irregular in shape with an average diameter of about 0.00001 inch.

Reticular Layer

The portion of the derma below the thermostat layer is often called the *reticular layer* because of its network appearance. The fibers of the reticular layer are relatively large, but those of the thermostat layer are relatively much smaller. A large fiber differs from a small one merely in being made up of many more fibrils. When the fibroblasts, in the course of their outward migration, reach the thermostat layer, it is assumed that many of them meet resistance and die. It may be that they decompose and are absorbed by the tissues. In any case, the fibers become smaller as they approach the outer surface of the derma. Fig. 8 shows a horizontal section of call leather cut only 0.00059 inch thick, but including the grain surface, the fibers of which appear to consist of from only one to several fibrils.

As the animal approaches maturity, the number of fibroblasts entering the hide decreases. The writer has always found them to be abundant in calf skins and almost entirely absent from full-grown hides. However, when the hide of a full grown animal is injured, as by burning or cutting, myriads of fibroblasts migrate to the seat of the wound, spinning out collagen fibrils as they go. At the site of the

wound they continue to spin fibrils until the wound is protected by an efficient mass of scar tissue, which is made of the same material as the hide fibers. When the fibroblasts continue to spin out collagen fibrils in excess of those needed, the result is a *fibroid tumor*.



Courtesy The Leather Manufacturer.

Fig. 8. Horizontal Section of Calf Leather including Grain Surface.

Location: butt.

Thickness of section: 15 microns, or 0.00059 inch.

Magnification: 200 diameters.

Fibroblasts

Fibroblasts are single living cells that appear to change their shape to suit their environment. When they are traversing a hide fiber in the act of adding another fibril, it is difficult to see them under the microscope with any sharp definition. Fig. 9 shows a vertical section of the reticular layer of a calf skin taken at a magnification of 170 diameters. The fibroblasts appear merely as dark dots scattered among and on the fibers, but they are not sharply defined. In studying pieces



Fig. 9. Vertical Section of Reticular Layer of Calf Skin.

Location: butt. Thickness of section: 20 microns, or 0.00079 inch. Magnification: 170 diameters.

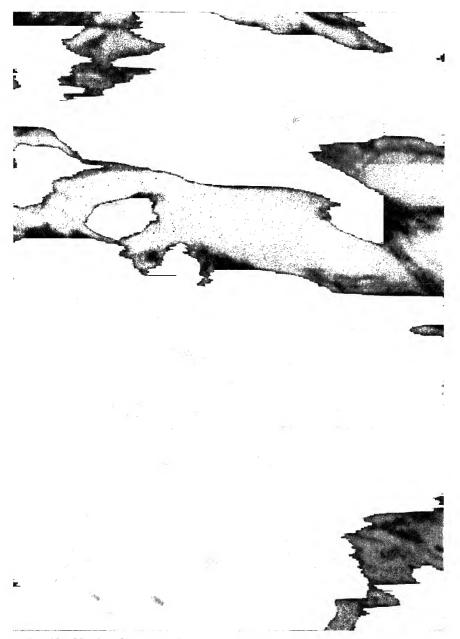


Fig. 10. Vertical Section of Scar Tissue Forming in Wounded Rabbit Muscle.

Location: muscle tissue. Thickness of section: 15 microns, or 0.00059 inch. Magnification: 3500 diameters.

of skin taken from people badly burned, the writer has observed fibroblasts in large numbers migrating to the burned regions. By studying the development of scar tissue in wounded rabbit muscle, the writer was able to catch the fibroblasts at work in the spinning of their collagen fibrils. A cross-section of scar tissue with the fibroblasts at work is shown in Fig. 10 at a magnification of 3500 diameters. Their thicknesses vary from about 0.0001 to 0.0006 inch and they vary greatly in shape. Just below the center of the picture, one of them appears rather sharply defined and pear shaped.

Adipose Tissue

Although the adipose or fatty tissues of hides are most frequently found in the flesh layers, they often develop as a part of the reticular layer itself and cause tanners a great deal of trouble. A vertical section of the adipose tissue of calf skin is shown in Fig. 11. The adipose tissues must not be confused with the sebaceous glands simply because they both contain fats. They are distinctly different in origin, method of growth and in structure. Unlike the cells of the sebaceous glands, the cells of the adipose tissue have no life and do not reproduce themselves, but, like the collagen fibrils, they are produced by migrating cells which do not form a part of the finished structure.

Fig. 12 shows adipose tissue of the reticular layer of a piece of human skin photographed at a magnification of 1680 diameters. It looks like the cross-section of a honey comb. The cell walls are built of protein tissue and the cells are not made up of nuclei and protoplasm for reproduction, but are merely filled with fatty material. Just above the center of the picture, there can be seen one of the cells which manufacture adipose tissue. It appears to be in a stage of reproduction. The writer suspects that these cells take rich carbohydrates and other materials from the blood for their own reproduction, migrating as they reproduce and exuding protein which sets into the cell walls of the adipose tissue, and exuding also the fatty materials which are emptied into the cells as they are formed. In hog skin, to be described later, the reticular layer is made up almost entirely of adipose tissue and has practically no hide fibers, all of the leather forming portion of the hog skin being in the thermostat layer. The cells that produce adipose tissue apparently become very active whenever the blood becomes rich in materials that can be converted by them into adipose tissue, which acts as a storage for excess food. This is conserved by the body in this way, when it is plentiful, against the possibility of a famine at some later time. A man developing a sizable panich may take comfort in knowing how it grows and why.

Blood Vessels

Animal hide contains a complete system of blood vessels, but those in the thermostat layer are often a source of considerable loss to the tanner because of the unsightly patterns that they may cause to appear on the grain surface of his leather. The arteries and veins are the body's piping system for blood. An artery consists chiefly of a tube of non-striated muscle tissue lined on the inside with epithelial tissue and on the outside with connective tissues. The muscular tissue of a vein is much thinner than that of an artery of the same capacity; this is responsible for the fact that a vein collapses when emptied, in contrast to an artery, which retains its shape. At the top of Fig. 11, an artery can be seen to the left and a vein to the right. The veins are equipped with semilunar valves, which prevent backflows of blood. There are network systems of trunk line blood vessels in and close to the flesh region of a hide. The only blood vessels in the reticular layer appear to be



Fig. 11. Vertical Section of Calf Skin Showing Adipose Tissue in Flesh Layer.

Location: butt.

Thickness of section: 20 microns, or 0.00079 inch. Magnification: 70 diameters.

thermostat layer. There are two systems of blood vessels in the thermostat layer: one close to the outer surface of the hide which supplies food to the sebaceous glands and the epithelial tissues, and the other much more deeply seated which supplies the sweat glands.

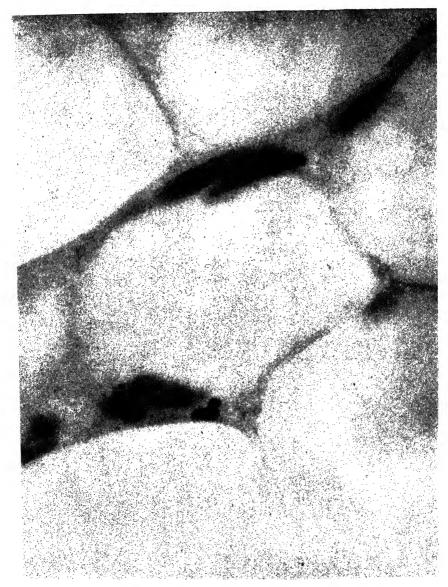


Fig. 12. Vertical Section of Adipose Tissue of Human Skin.

Location: chest.

Thickness of section: 10 microns, or 0.00039 inch.

Magnification: 1680 diameters.

Elastin

The thermostat layer contains also another type of connective tissue called yellow, composed of the protein substance clastin. It differs markedly in its properties from the rehite connective tissue collagen. Elastin fibers are found in abun-

dance in the thermostat layer, in the flesh layer and surrounding all blood vessels, but not in the reticular layer except when associated with blood vessels. The elastin fibers seem to consist of individual fibrils and not of bundles, as in the case of the collagen fibers. They appear to perform a service like that of structural steel-work in a building. They act as a support for the blood vessels and appear to furnish the rigidity of structure needed for the proper functioning of the erectorpili muscles. They appear very plainly in Fig. 3 as thin, sharply defined black lines many of which are attached to the erector-pili muscles.

When a hide is immersed in either an alkaline or an acid solution, the collagen fibers swell by absorbing water, which causes the hide to become plump and rubbery. The elastin structure, however, resists this swelling; this causes indentations in the grain surface of the hide following the pattern of the blood vessels in the sebaceous-gland level. If the hide is permitted to swell unduly, permanent strains occur close to the grain surface which cannot later be corrected, and the finished leather appears grainy. This may cause the money value of the leather to drop to an amount less than was paid for the raw hide.

Seasonal Differences

The skins of calves slaughtered in the northern part of the United States during the coldest months of the winter show much more of this undesirable grainy condition than those of similar calves slaughtered in the hot summer months. Where only 2 per cent of stock might have to be put into the grainy grade for skins of August slaughter, the figure might run to 30 per cent for similar skins of February slaughter.

This was found to be due to the fact that six-weeks old calves slaughtered in February had spent all their lives in cold weather; the blood vessels in the sebaceous-gland layer of their skins were highly developed, tending to exaggerate the grainy appearance of the grain surface of the finished leather caused by the blood vessels of the sebaceous-gland layer during periods of the swelling of the rest of the skin. Even with older animals, hides of summer slaughter are to be preferred for leather making to those of winter slaughter. In winter the animals may not be as well fed as in summer, and the sebaceous glands therefore require a greater proportion of the available food supply of the skin.

Nerves

Animal hide also contains an elaborate system of nerves, most of which seem to function in the region where the epidermis and derma come together. Like the blood vessels, trunk-line nerves are found in the flesh and again in the thermostat layer, the only ones in the reticular layer appearing to be those connecting the nerves of the flesh layer with those of the thermostat layer.

Fig. 13 shows a cross-section of a nerve found in human skin taken from the calf of the leg and magnified 100 diameters. The whole nerve appears as a long cord which branches like a blood vessel, finally ending in an enormous number of terminals from which the sensations are carried back through the system to the spinal cord and on to the brain. The nerve shown in the picture consists of a number of separate systems of nerves bound stoutly together with connective tissues. The individual systems are also separated from each other by connective tissues. Among the connective tissues, cross-sections of both arteries and veins may be seen. Near the center of the picture a large vein may be recognized by its collapsed condition; the arteries may be identified by their thick muscular walls which prevent them from collapsing. The nerve tissue itself is made up of an exceedingly

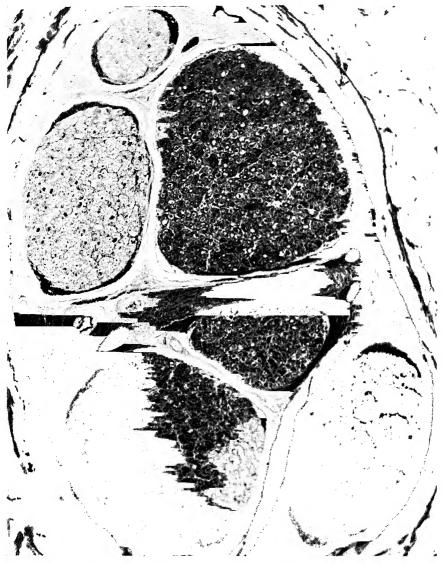


Fig. 13. Vertical Section of Nerve of Human Skin.

Location: calf of leg.

Thickness of section: 20 microns, or 0.00079 inch. Magnification: 100 diameters.

complex system of cells, which we cannot undertake to discuss in a book of this kind. Surrounding the nerve cord itself, adipose tissue may be seen. All the reticular layer of this specimen of skin was composed primarily of adipose tissue, with only a few strands of connective tissue traversing it.

The nerves of the skin are of very great importance to the whole body. The pilo-motor nerves, which are sensitive to temperature changes, control the thermostat mechanism. The nerves sensitive to harmful ultraviolet light rays cause a rush of blood to the epithelial cells of the epidermis, furnishing them with coloring matter capable of filtering off the ultraviolet rays so that they cannot destroy the delicate mechanisms below. Nerves in the skin furnish us with the sense of touch and warn us of unfavorable environments. There are nerves that tend to counteract the effects of sudden shock, anger, fear and other disagreeable states.

Where the epidermis is very thick, portions of the derma containing nerve ends project into it. These are called *nerve papillae*, and they are found wherever the nerve senses of the skin are highly developed, as in the fingers.

Hyaline Layer and Sheaths

Animal hide also contains blood, many soluble proteins and various salts. There has been much controversy over the existence of special tissues, not readily seen, at the surfaces of well recognized tissues. For example, Seymour-Jones reported the existence of a tissue between the collagen fibrils of the grain surface and the lowest layer of epithelial cells of the epidermis which he called the *hyaline* layer; but Küntzel denied the existence of such a layer. Certainly it cannot be seen in an ordinary cross-section of hide at the highest magnification possible; but Turley, using a special technic on sections of steer hide which had been limed and unhaired, found a layer of something on the surface of the derma that stained differently from collagen and which he believed was the elusive hyaline layer. He also found evidence for the existence of *areolar-tissue sheaths*, in which the collagen fibers are enclosed. Seymour-Jones had previously reasoned that the collagen fibers were enclosed in very thin sheaths of what he called *fiber sarcolemma*.

Reticulin

When fibers separated from a hide are placed in acid or alkaline solutions, they swell by absorbing water and increasing in volume, but marked constrictions occur at points along the length of the fiber. Kaye has shown that these are caused by delicate threads of the protein reticulin, which appear to bind the collagen fibrils together in a fiber and even appear to bind numbers of fibers themselves together. The proportion of reticulin to collagen appears to be greater in the looser portions of a hide. Reticulin is much more resistant to the action of acids and alkalies than collagen, although it may be attacked by the action of bacteria in soak waters. It is readily attacked by pepsin, but not by pancreatic trypsin. Unlike collagen, it does not dissolve readily in boiling water. The fate of the reticulin threads during the tannery operations probably plays a large part in determining the properties of the finished leather.

Grain Surface

The fibrils that make up the grain surface of the leather have been supposed to be a continuation of the collagen fibrils of the reticular layer, but they differ from it in many ways. If calf skin is put into a solution of caustic soda strong enough to destroy most of the collagen fibers, epidermis and hair, the fibrils of the grain surface are left apparently unharmed. When a piece of bated skin is placed in boiling water, the fibrils of the grain surface remain as a thin sheet after the bulk of the skin has passed into solution as gelatin. They are unaffected by treatment with pancreatic enzymes strong enough to dissolve all the elastin fibers below them. However, they are rapidly destroyed by bacteria in contaminated tannery soak water, suggesting a possible relation to reticulin.

It may be that the same fibroblasts produce different kinds of related protein tissues dependent upon environment and available food supply or there may be different kinds of fibroblasts at work in the skin. The protein tissues themselves apparently change with age, the older tissues being more resistant to some types of destruction than the younger ones.



Fig. 14. Horizontal Section of Cow Hide Cut in Plane of Sebaceous Glands

Location: hind shank.

Thickness of section: 20 microns, or 0,00079 inch.

Magnification: 48 diameters.

Horizontal Sections of Cow Hide

In order to get a full appreciation of the structure of a hide in three dimensions, it is necessary to study both vertical and horizontal sections. Fig. 14 shows a

horizontal section of cow hide cut in a plane passing through the sebaceous glands and 0.021 inch below the outer surface of the epidermis. The entire area shown is only 0.009 square inch. Many hairs can be seen running in a direction perpendicular to the plane of the page. Each is surrounded by a thick layer of epithelial



Courtesy The Leather Manufacturer.

Fig. 15. Horizontal Section of Cow Hide Cut in Plane of Epidermis,

Location: hind shank.

Thickness of section: 20 microns, or 0.00079 inch.

Magnification: 175 diameters.

tissue. Between the hairs can be seen the sebaceous glands, blood vessels, collagen fibers and elastin fibers. When the hide as a whole becomes excessively swollen or plumped by the action of acids or alkalis, the collagen fibers increase in volume by absorbing water, but the elastin fibers swell very little. This causes a condition of tension and results in the formation of indentations of the grain surface following the pattern of the elastin fibers. These fibers show in the picture as thin black

lines. By following the arrangement of the elastin fibers, the tanner can recognize the pattern of the rough or wild grain resulting from improper liming and bating.

Figs. 15, 16, 17 and 18 form a series, all including the same hair. Fig. 15 was cut in the plane of the epidermis. In the center can be seen the hair follicle, oval in shape, containing the hair in its lower half. The oval-shaped mass around



Courtesy The Leather Manufacturer.

Fig. 16. Horizontal Section of Cow Hide Cut in Plane of Ducts of Schaceous Glands.

Location: hind shank.

Thickness of section: 20 microns, or 0.00079 inch.

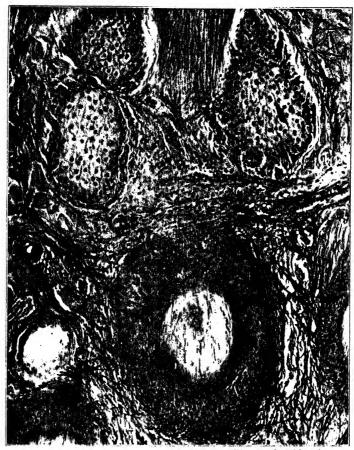
Magnification: 175 diameters.

the hair is the hair sheath, consisting of epithelial tissue which is continuous with the epidermis. The dots to left and right are the nuclei of the cells of the epidermis. The light patches below the hair sheath are nerve papillae, which in the cow are present only in the shanks and for which reason these sections were taken from the hind shank.

Fig. 16 was cut in the plane 0.012 inch below that of Fig. 15. This is the

plane where the ducts of the sebaceous glands enter the hair follicle. The elastin fibers appear as sharply defined black lines and the collagen fibers as larger structures much lighter in color. Portions of sebaceous glands can also be seen.

Fig. 17 shows the same hair in the plane 0.009 inch below Fig. 16, or 0.021 inch below Fig. 15. This is the same plane as that of Fig. 14. Here the thick



Courtesy The Leather Manufacturer.

Fig. 17. Horizontal Section of Cow Hide Cut in Plane of Sebaceous Glands.

Location: hind shank.

Thickness of section: 20 microns, or 0.00079 inch.

Magnification: 175 diameters.

hair sheath tightly surrounds the hair. Directly above the hair, at the top of the picture, is a portion of the erector-pill muscle and the sebaceous glands stand out sharply to its right and left. The elastin fibers stand out sharply as thin black lines.

Fig. 18 was cut right through the bulb of the hair in a plane 0.033 inch below that of Fig. 15. All around the hair bulb are the empty sacs that contained the



Fig. 18. Horizontal Section of Cow Hide Cut in Plane of Hair Bulbs and Sweat Glands.

Location: hind shank.

Thickness of section: 20 microus, or 0.00079 inch.

Magnification: 175 diameters.

sweat glands. In this plane there are very few elastin fibers; nearly all of them are to be found between this plane and that of Fig. 15.

Calf Skin

Fig. 19 shows a vertical section of ealf skin taken from the butt area of a healthy heifer. The thermostat layer occupies a greater proportion of the total thickness than in the cow hide. Apparently a minimum thickness of thermostat layer is required for its proper functioning. The thermostat layer of a guineapig skin is just as thick as that of a calf skin; thinner skins or thinner parts of the same skin simply have thinner reticular layers. As a rule, the skin of a heifer calf has greater fulness and fineness of appearance than that of a steer calf.

Flesh

The flesh layer shown in this picture is much thicker than that of the cow hide shown in Fig. 1, but this is due merely to differences in flaying. Fig. 11 shows the flesh layer of calf skin at higher magnification. It consists of both adipose and areolar tissues. The areolar tissues consist simply of collagen and elastin fibers, loosely arranged, which connect the skin with the underlying parts of the body. The adipose tissues are those containing fat cells; they are often found in the flesh, but sometimes also in the reticular layer of the skin. They must not be con-

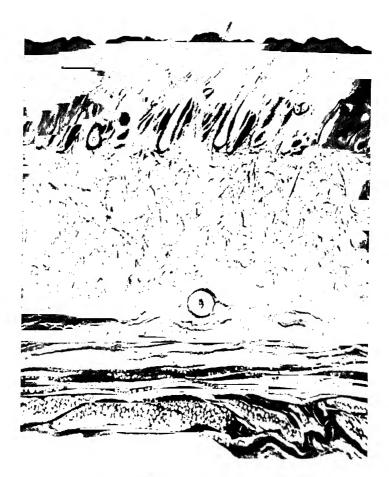
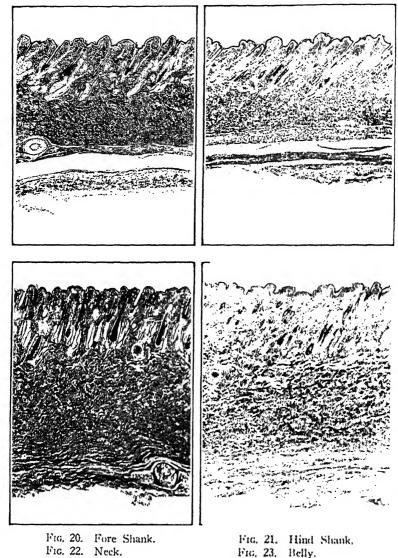


Fig. 19. Vertical Section of Calf Skin.

Location: butt.

Thickness of section: 20 microns, or 0.00079 inch.

Magnification: 30 diameters.



Vertical Sections of Calf Skin.

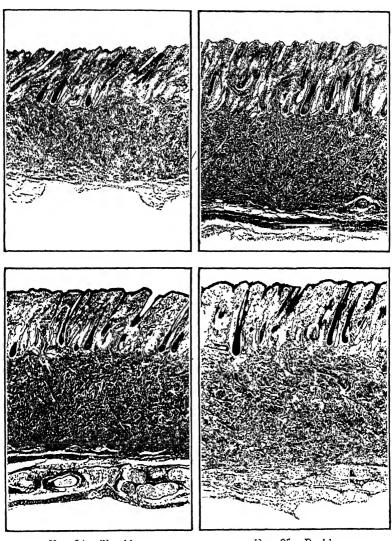
Location: as noted. Thickness of sections: 15 microns, or 0.00059 inch. Magnification: 15 diameters.

fused with the sebaceous glands, from which they differ sharply in origin and composition.

At the middle of the lower end of the derma can be seen the cross section of a large artery with its shape maintained by the heavy wall of muscle tissue. To the right of it is the cross section of a nerve.

Variations Over Skin Area

The thickness of the reticular layer of a skin varies over its entire area. Similar variations occur also in the compactness of the fibrous structure. These variations for the calf skin are shown in Figs. 20 to 27, inclusive. They were



Frg. 24. Shoulder. Frg. 26. Butt.

Fig. 25. Backbone. Fig. 27. Tail.

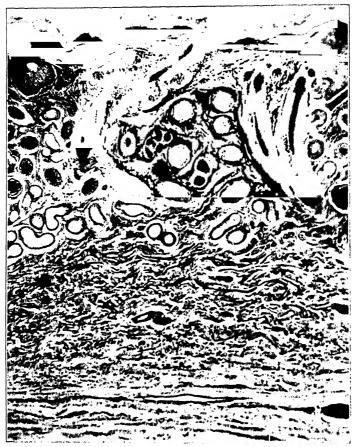
Vertical Sections of Calf Skin.

Locations: as noted.

Thickness of sections: 15 microns, or 0.00059 inch.

Magnification: 15 diameters.

taken, for convenience of presentation at the low magnification of only 15 diameters and can reasonably well be compared with the section of cow hide shown in Fig. 1 at 16 diameters. In making comparisons of photomicrographs in this book, great care must be taken to take the magnifications into consideration.



Courtexy The Leather Manufacturer.

Fig. 28. Vertical Section of American Sheep Skin.

Location: butt.

Thickness of section: 20 microns, or 0,00079 inch. Magnification: 50 diameters.

It will be noted that the thermostat layer is of the same thickness in all parts of the skin, but the reticular layer is nearly three times as thick in the butt as in the hind shank. In the shoulder, the reticular layer is thinner than that of the butt and its fibers are finer. In the belly, the collagen fibers run nearly horizontally, but in the butt, they run more nearly vertically. The grain surface appears less serrated on the butt than elsewhere. By studying these eight pictures very care fully, a better appreciation can be obtained of the wide variation of the physical properties of leather over the area of a hide or skin.

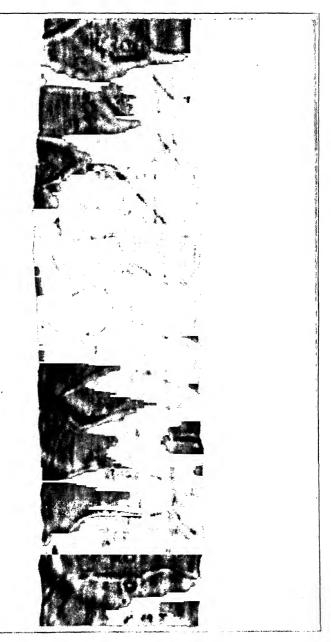


Fig. 29. Segment of Sheep Wool. Magnification: 1260 diameters.

Sheep Skin

Fig. 28 shows a cross-section of the butt portion of a skin from a healthy sheep native of the United States magnified 50 diameters. Its structure presents a marked contrast to that of the calf skin and explains why the properties of sheep leathers are so different from those of calf. Differences in the thermostat layers are very marked. The sheep has many more sweat glands and sebaceous glands, suggesting that it is much better prepared to withstand extreme changes of temperature. The crowding of these glands causes a distortion of the hair follicles. During the development of a hair by reproducing epithelial cells, the follicle acts as a mold, giving to the hair its shape. Since straight hair is formed only by straight follicles, the sheep grows curly hair or wool simply because its follicles have been curved or distorted in shape by the crowding of the glands in the course of their rapid reproduction. In its formation the wool also acquires a scaly surface which assists in giving it felting properties. This is shown in Fig. 29.

It will be noted that the thermostat or grain layer of the sheep occupies more than one-half the total thickness of the skin. In the reticular layer, the collagen fibers are not compact, as in the calf, and they run in more nearly horizontal directions.

The proportion of adipose tissue to collagen fibers in sheep skins varies considerably according to the feeding of the animal, and there is often an almost continuous layer of fat cells separating the thermostat and reticular layers. Because much of the fatty tissue is destroyed or removed in the beamhouse operations, it is not uncommon to find the thermostat and reticular layers of sheep leathers separated over wide areas. Sometimes tanners separate these two layers by splitting after liming, and then tan the grain layers for leather for hat bands, bookbinding, etc., and the reticular layers for chamois leather.

During the beamhouse operations, the glands in the thermostat layer are destroyed, and this leaves the grain layer rather spongy in structure. This, together with the relatively loose and empty structure of the reticular layer, puts sheep leathers in a class by themselves. They make ideal garment leathers and are used to a considerable extent for shoe linings and for boxing gloves.

Goat Skin

In many respects the skin of the goat may be regarded as having a structure intermediate between that of the calf and the sheep. The fibers are fuller and firmer than those of the sheep, but not as numerous nor as compact as those of the calf. A fully matured goat has a skin much smaller than that of even a six weeks old calf.

Fig. 30 shows a cross-section of domestic kid skin magnified 50 diameters. Nearly all the goat skins tanned in the United States are imported from foreign countries and most of them are dried hard before shipping to preserve them and to decrease the shipping weight. A domestic skin was chosen for presentation in the picture because it could be obtained in a fresher condition and a better photomicrograph made from it. The thermostat layer of the kid skin occupies well over one-half the total thickness of the skin, but the glands and fat cells responsible for the sponginess of sheep leather are much less abundant in goat skins.

Because of the lesser development of glands, the goat, like the calf, has straight hair follicles and so grows straight hair. The epidermis is the very thin dark line forming the upper boundary of the skin. It dips down into the derma, forming a nearly straight follicle, which it lines and in which the hair grows. The erector pili muscle is the thin line running upward to the right from the base of the follicle. The opening of the sebaceous glands into the follicle can be seen just above

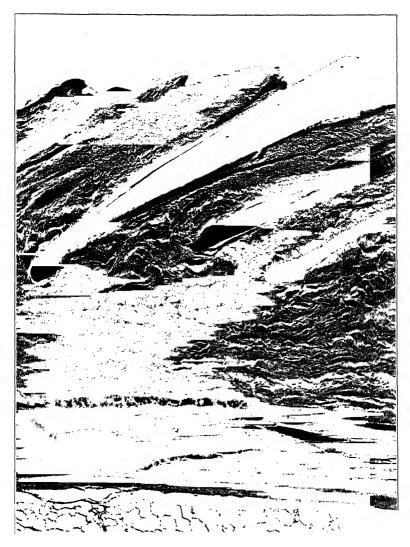


Fig. 30. Vertical Section of Kid Skin.

Location: butt.

Thickness of section: 25 microns, or 0.00098 inch.

Magnification: 50 diameters.

the crector-pili muscle. Even in the butt of the goat skin, the collagen fibers of the reticular layer tend to run horizontally, as in the belly of the calf skin.

Bounding the lower surface of the derma is a layer of striated muscle tissue, which permits the animal to twitch its skin to shake off flies. Muscles of this kind are often found as part of the flesh of many animal hides. Above and below the muscle may be seen renmants of adipose tissue.

Hybrids

Because goat skins come from so many different countries, they vary greatly in their suitability for making specific kinds of leather. In China, it is common practice to use male goats to guard the sheep, and there is much interbreeding and the progenies are straight-haired sheep. On a trip to China, Mr. Charles B. Simmons, Jr. secured for the writer a specimen skin from one of these straight haired sheep, quite typical of the great Chinese herds. A cross section from the butt is shown in Fig. 31 at a magnification of 25 diameters. The structure represents a fairly good average of the structures of both goat and sheep. The thermo stat layer of this specimen is twice as thick as the reticular layer, and the two layers show a marked tendency to separate. Practically all the tissues can readily be identified from the general discussions of histology given above. This type of hybrid is known as a cabretia.



Fig. 31. Vertical Section of Chinese Sheep Skin (Cabretta).

Location: butt.

Thickness of section: 20 microns, or 0.00079 inch

Magnification: 25 diameters.



Courtesy The Leather Manufacturer.

Fig. 32. Vertical Section of Horse Hide.

Location: butt.

Thickness of section: 20 microns, or 0.00079 inch.

Magnification: 20 diameters,

Horse Hide

The outstanding peculiarity of horse hide lies in the reticular layer. In the butt area, there is a dense mass of collagen fibers so compact as to render leather made from it nearly air-tight and waterproof. Fig. 32 shows a cross-section taken from the butt of a horse hide at a magnification of 20 diameters. The dense mass of fibers, often called the *glassy layer*, can be seen running horizontally across the reticular layer and appearing much darker in the picture than the rest of the reticular layer. Only the butt area of the hide contains this glassy layer, and it is known as the *shell*. Leather made from it is called *cordovan* and sometimes *shell cordovan*, as a double assurance that the shell of the horse hide was used. It takes its name from the province of Cordoba in Andalusia, Spain, once famous for this kind of leather. Although the butt area of the horse hide is extreme in its tight-

ness and solidity of structure, all the rest of the hide is extreme in its looseness for a large hide.

In making cordovan leather, it is customary to split the shell into two layers right through the middle of the glassy layer and to finish the leather on the split side so that the glassy layer itself is exposed in wear.

Hog Skin

In the United States, when hogs are slaughtered, it is customary to leave the skin on the meat; therefore relatively few domestic skins are available for tanning. However, there are strips of skin from over the lard areas that form a by-product of the packing industry that are tanned to make shoe counters and other articles not requiring great area. Most of the whole domestic skins that become available for tanning are of low quality because of grain damage and poor flaying. There



Fig. 33. Vertical Section of Hog Skin.

Location: butt, Thickness of section: 20 microns, or 0,00079 inch. Magnification: 20 diameters. is a demand for hog skins for leather for saddles, hand bags, etc., but the best skins are obtained from foreign countries.

Fig. 33 shows a cross-section of the butt of a domestic hog skin at a magnification of 20 diameters. It differs from other skins in a number of ways. The reticular layer consists almost entirely of adipose tissue, which extends well up into the thermostat layer. Since the adipose tissue is removed preparatory to tanning, the hair follicles in hog leather appear as though they completely passed through the skin, but this is not so. Apparently hair follicles never penetrate quite to the bottom of the true skin in any animal, although the leather gives that appearance whenever all the reticular layer and a part of the thermostat layer consists of adipose tissue.

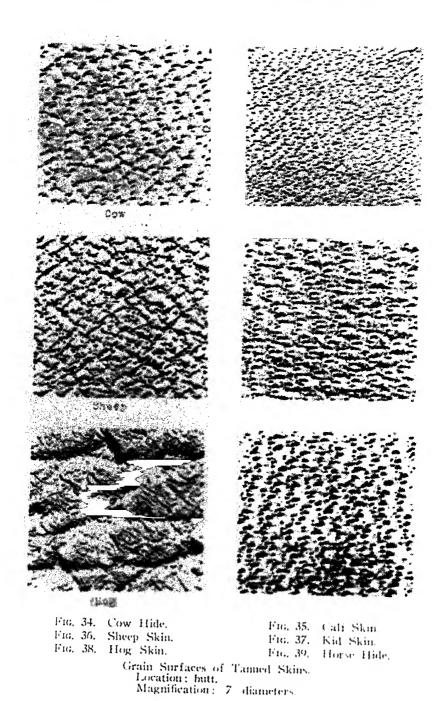
The hair follicles of the hog are unusually large; they cause the hair to grow so large in cross-section that they are referred to as bristles. The sweat glands develop in adipose tissue and the sebaceous glands are not highly developed. Instead, the thermostat layer contains a high development of collagen fibers. The epidermis is unusually thick and nerve papillae project into it at rather short intervals, contributing to the roughness of grain surface of hog leathers. The hairs, being large, offer an opportunity to study the hair papillae in detail. Even at the relatively low magnification of 20 diameters, the hair papilla can be seen very plainly. The bottom end of the hair bulb appears like a pair of pincers with the jaws slightly open and facing downward. Passing through the opening in the jaws into the large open space above and resembling a candle flame in shape is the hair papilla, which contains blood vessels which supply food to the reproducing epithelial cells that eventually form the hair.

Grain Patterns

The design of the grain surface of leather not altered in any way is distinct for each species of animal, and the fineness of pattern is an indication of the age of the animal. Each pattern is a composite of the openings of hair follicles and pores, the presence or absence of nerve papillae and the effects of structures of thermostat layer and epidermis. Figs. 34 to 39, inclusive, show grain-surface patterns of the cow, calf, sheep, kid, hog, horse, camel, bear, guinea-pig, horned toad, albino rat and salmon, respectively, all photographed at exactly the same magnification of 7 diameters.

The number of hair follicles per square inch of hide surface varies not only with the species and age of an animal, but also over the area of a single hide; consequently, comparisons according to age for the same kind and breed of animal can be made reliably only when the specimens for examination are taken from exactly corresponding locations on the hide. This was done for the calf and cow specimens shown in Figs. 34 and 35. Both were taken from corresponding points of the butt area.

Taking into consideration the fact that one square inch of picture represents only $\frac{1}{4}$ th square inch of actual hide surface, it will be noted that one square inch of actual calf leather shows about 16,000 hair follicles, but one square inch of actual cow leather shows only about 5,000. The calf skin had an area of about 12 square feet and the cow hide about 38 square feet. The cow hide thus had an area about 3.2 times as great as the calf skin and the calf skin had about 3.2 times as many follicles per square inch of surface. This confirms the writer's theory that an animal is born with all the hair follicles it will ever have. As the surface area of an animal increases during its growth, the cross-section areas of the follicles increase and hairs of correspondingly increased cross-section areas are produced, but the total number of follicles apparently does not change. Some hair follicles



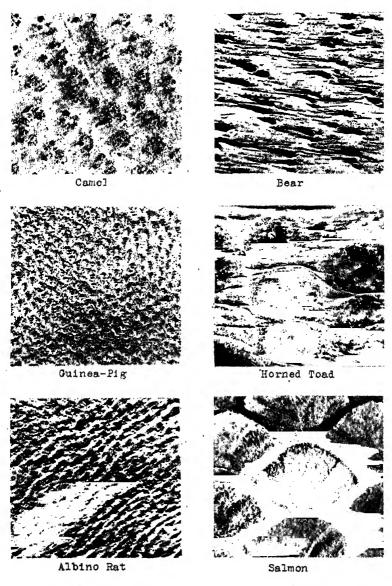


Fig. 40. Camel Hide.

Fig. 42. Guinea-pig Skin.

Fig. 44. Albino-rat Skin.

Fig. 41. Bear Skin.

Fig. 43. Horned-toad Skin.

Fig. 45. Salmon Skin.

Grain Surfaces of Tanned Skins. Location: butt. Magnification: 7 diameters. may remain in a nearly dormant state until the age of puberty is reached, when a marked increase in available food supply occurs; but the follicles probably were present at the moment of birth.

The rough pattern of the sheep grain surface reflects the spongy thermostat layer and curved hair follicles below, and that of the hog the large follicles and nerve papillae. The kid and horse show the peculiar tendency of these animals to have large and small hair follicles arranged in characteristic patterns. In fish, the hairs are called scales because of their shapes, in which one dimension of a crosssection is very much greater than the other.

What is known of the subject matter of this chapter would fill many large Hundreds of volumes could be written on all the phases of leather manufacture. In order to present those interested in leather with an easily readable work, it has been felt necessary to limit the presentation to the minimum that a successful tanner should know, indicating so far as is practical where he can find such further information as he may desire. It is hoped that the curiosity of many readers will be aroused to the point that they will master the technic necessary to independent studies of the histology of animal hide and add to the general knowledge.

The references given at the end of this chapter are far from complete, but they will enable the reader to get a better view of both sides of controversial points and to learn more about the general subject.

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Chapter 2

Preparing Hides for the Market

In the largest packing plants in the United States, every detail of work involved in the slaughter and flaying of the animals and in the curing and bundling of the hides has become highly specialized. In flaying an animal, the work is done by a dozen or more highly skilled butchers, each a specialist in one single operation. One result is that flaying damage is reduced to a minimum and the hide is cut to a correct pattern. The pattern of a hide is its contour when laid flat on the floor, flesh side up. The outline of a hide of correct pattern is shown in Fig. 46. Another result is that the curing of the hide is done more efficiently and there is less damage from putrefaction. The hides from these huge plants are known as big-packer hides, and they have become the standard for pattern and condition by reason of the highly specialized nature of the workmanship in the complete removal of the hide and its subsequent curing. Each workman performs only a small part of the work. The repeated skinning of only one portion brings his work closer to perfection than is possible when the same man performs a number of different operations. Since any defects in flaying lower the value of a hide for making leather, the big-packer hide is taken as the standard in workmanship.

In the smaller packing plants, fewer workmen are available to perform the operations and the same degree of perfection is not reached. Hides from the smaller plants are known as *small-packer* hides. Next below these in quality are the *city-butcher* hides. The larger animals are usually flayed in the city abattoirs; if there are several abattoirs in a city, the work of flaying may be pooled and all done at one plant for greater efficiency. Calves are often delivered cold to local butchers, who really cut the meat out of the cold skin. The skins are kept cold and accumulated until collected by dealers who take them to special plants for curing.

At the bottom of the list are the *country* hides, which vary greatly in quality. The animals may be of as good grade as those in the large packing plants, but the flaying may be done by an individual farmer or by a country butcher and much damage may result from lack of skill and experience. The hides are often badly cut, scored and of poor pattern. As they may be sold without proper curing to small collectors who, in turn, sell them to larger dealers, they may come to the tanners with putrefactive as well as flaying damage. They present much more of a gamble to tanners who are not fully aware of their histories, but their price is correspondingly lower than that of packer hides; and clever tanners, knowing how and where to buy them and how best to handle them upon arrival, have been able to make them a source of considerable profit.

A great contribution to the literature on hides was recently made by James Price, Jr. in his book "North American Packer Hides," published by Pratt Bros. Co., New York and Chicago, publishers of *Pratt's Reports* and the *Daily Hide and Leather Market*. We are indebted to Pratt Bros. Co. for permission to quote freely from this book and for the use of the cuts shown in Figs. 49 to 54, inclusive.

Slaughter

In a big packing plant, the cattle are driven into knocking pens, where the knocker stuns each one by a blow on the forehead with a light sledge. This crushes the bone into the brain structure and renders the animal oblivious of the subsequent slaughtering operations. The stunned animal is then dumped onto the killing floor

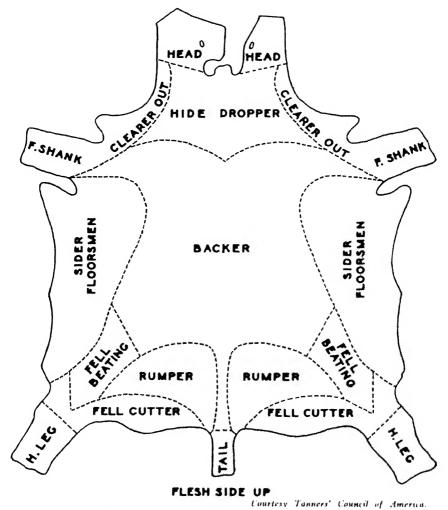


Fig. 46. Correct or Standard Pattern (Outline) of Big packer Hide Showing Areas of the Different Butcher Operations in Flaying.

and shackled with a heavy chain around one or both hind legs. It is then hoisted to an overhead rail and hung-off, head downward to await the *sticker*, who inserts his knife into the *develap*, or *sticking piece*, in the center of the neck, where such a cut will not mar the pattern of the hide, and severs the jugular vein. The blood

is then drained from the animal. At this point, the animal is dead and the process of flaying, or removing the hide begins.

Flaying

The first operator is the *header*, who approaches the animal, still hanging head downward and draining, and inserts his knife at the top of the head towards his left and cuts across the top of the animal's face, continuing downward along the left side, at the same time skinning out the pate and face of the animal. The cheeks are then skinned out and the neck is opened up from the sticking cut through the center of the lower lip. The top spinal-column joint is then severed and the skull dropped to the floor.

The carcass is then moved by conveyor to the *skinning bed*, lowered to the floor and placed on its back and held upright by means of a *pritch pole* placed just behind the foreleg and against which the carcass rests. The *leggers* then skin out the fore and hind legs and remove the shin bones with hoofs attached; the legger cuts the sinews, or tendons, joining the hoof to the leg, at the back of the hoof. Cutting off the *dewclaws*, the legger opens up the shanks with an upward cut from the hoof to the back of the knee.

While still in the *pritched* position, the carcass is opened at the belly from the sticking piece to the tail. The *floorsman* then starts working on the side opposite the pritch pole. He inserts his knife between the beef and the hide at the center of the belly to start removing it from the sides of the animal. His knife-work determines whether the hide will be of good pattern and free from defects in its most valuable portions. He starts removing the hide at the forequarter by starting his cut well forward on the brisket in advance of the foreleg and cuts backward on a slant to the back of the foreleg knuckle.

In opening up the hide at the butt, the floorsman starts cutting upward from the opened center cut, beside the bag in cows or scrotum in steers, and about 6 or 8 inches from the tail, depending upon the size of the bullock. This cut is continued upward to join the cut of the hind-legger at the back of the knee joint. Having completed the skinning of one side, the floorsman rocks the carcass to change the pritch pole to the other side to permit the skinning of the opposite side.

While pritched up, the caul fat, sweetbreads and weasand are removed. The breast and aitch bones are sawed to facilitate separation of the carcass into two sides of beef later. The carcass is then hoisted slightly by hooks placed in the hind-leg gams to permit skinning out the hind quarters. The tail-puller skins and pulls out the tail bone and the fell-cutter removes the hide from the hind legs at the round.

The rumper cuts the hide away from the base of the tail and rump. Fell-beaters then remove the hide where it adheres tightly at the front of the round and flank, beating it with the backs of cleavers as other workmen hold the hide taut and pull it from the beef in this area. This removes the hide down to the hips of the carcass, which is then raised to a half-hoist position, with the shoulder and neck on the floor, where entrails and pluck are removed and presented to the government inspectors to examine for disease. The backer then drops the hide from the base of the tail to the shoulders with cautious knife work. Splitters then sever the carcass into two sides as far down as the shoulders.

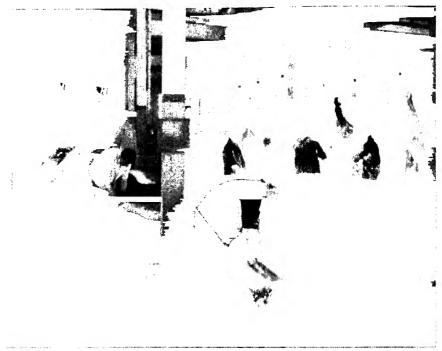
The carcass is then raised and hung-off on wheeled rail trucks, permitting the complete removal of the hide. The clearer-out skins the hide from the fore legs and under the sides of the neck, following which the hide-dropper removes the hide from the shoulders and remainder of the neck. The hide is then spread out on the killing floor, flood with the hide is then spread out on the killing floor.

are pointed out to the butcher causing them. The green hide, at this stage, weighs between 6 and 7 per cent of the animal's live weight.

The various operations involved in flaying can be followed in greater detail by studying Fig. 46. The contour of the hide shown represents the correct or standard pattern of a big-packer hide. Each outlined portion shows the area covered by an expert in the flaying of that particular area.

Fig. 47 is a photograph taken on the killing floor of a large packing plant show

ing various stages of the flaving operation.



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Fig. 47. Flaying Cattle Hides in Big-Packer Plant. On the left, cattle are shown on hang-rail, headed and draining of blood. In the foreground, a legger is skinning a hind leg. Just behind, a floorsman is starting his work. In the background other stages of the flaying can be seen.

Curing

After flaying, the green hide is dropped down a chute to the hide cellar. The operations of killing and flaying proceed so rapidly that the hide reaching the cellar still contains much of the animal heat; therefore it is allowed to cool for nearly two hours before curing is started. Workmen first inspect it for class, grade and weight and then trim off the snout, lips, ears, earbase fat and gristle to conform to standard practice. Because of the rapidity with which bacterial action sets in, it is important not to delay curing after the hide has cooled to room temperature. On the other hand, if curing is started before the body heat is dissipated, bacterial action on the hide is encouraged.

Building a Hide Pack

Price describes the details of the curing operations as follows: "The site selected for building the hide pack should have good drainage toward the front, with gutters or sewers covered with wood, and should be of fairly large area. This is necessary so that the curing shrinkages will not be excessive and hides will remain moist and in good merchantable condition. There is no hard and fast rule for pack size, but length should be about twice width, say 15 by 30 feet or 20 by 40 feet in area. Pack heights should not exceed four to four and one-half feet to secure the best results.



Courtesy Armour Livestock Bureau.

Fig. 48. Salting Hides in the Pack. Two hide spreaders hold hide on one of the side edges for the salt thrower to cover with salt.

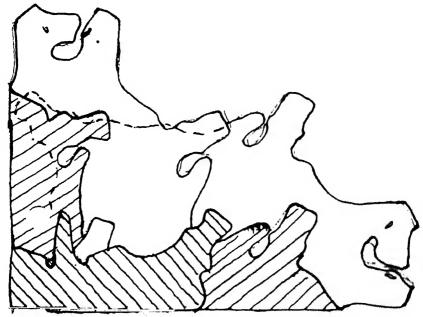
"It is well known that folded hides show a greater shrinkage in curing than unfolded ones. Therefore the larger sized packs have greater numbers of hides spread out flat in the fills than folded in the edges. Short, small or narrow packs, built to a height of more than five feet usually show excessive shrinkages. Also summer hides show larger shrinkages than those of winter production. Winter hides have longer hair to retain dirt and moisture, and the lower winter temperatures retard chemical action somewhat, although the big packers try to maintain uniform temperatures all year around.

"Having selected the spot where the pack is to be built, No. 2 size rock salt should be scattered liberally on the bare floor so that the hair side of the bottom layer of hides will be protected with brine, and also prevent the hides from sticking to the floor. As a further precaution in the preservation of hides, it is advisable to

build the packs level, to retard the run-off of brine, and hold shrinkages to normal. As a result, the hides remain merchantable longer and they do not dry out."

The Back Edge

"To start building the pack, it is necessary to place hides along the back and side edges to outline it. The first hide should be placed in one corner of the back edge, head to center. The two hide spreaders grasp the hide, folded flesh side in, by the shanks and the head or tail while carrying it to its position in the pack. The lower portion is dropped so that about three-fourths of the hide is on the floor. The remaining fourth is held upright by the shanks and belly while a third workman, the salt thrower, spreads No. 2 size rock salt uniformly upon the upturned flesh side. [See Fig. 48.]



Courtesy Pratt Bros. Co.

Fig. 49. Showing How First Hides Placed in Pack Outline a Back Corner.

"In making these back and side edges, it is good policy to let the upright held side extend or sag over the edge of the pack, when being held for the salt thrower. This permits a lot of salt to fill this lap, to be retained there to help build up the edge. Fold the edge of the hide over, allowing this sag to remain, and then gently pull shanks, head and belly toward the center of the pack until the edge is in its proper place.

"It is unwise to pull the top lap back, unless the entire hide is pulled with it, and even then there is danger of dragging salt off the hide underneath. This first hide placed in the pack should have but one fold and be laid full length as close to the corner as possible.

"The next hide is laid in the side edge, head toward the front, leaving enough of the butt beyond the back edge, so that it can be thrown over to form a corner.

[See Fig. 49.] In making this or any such corner, see that the flesh and hair sides of the overthrown portion are well covered with salt, and a generous quantity thrown into the *pocket* to make a strong corner.

"Having begun one back corner, the opposite one should be made, and then the entire back edge between them filled in, interlapping at the center to form a stable and uniform foundation."

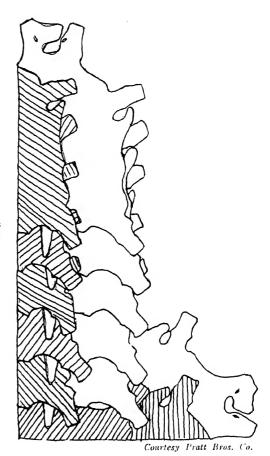
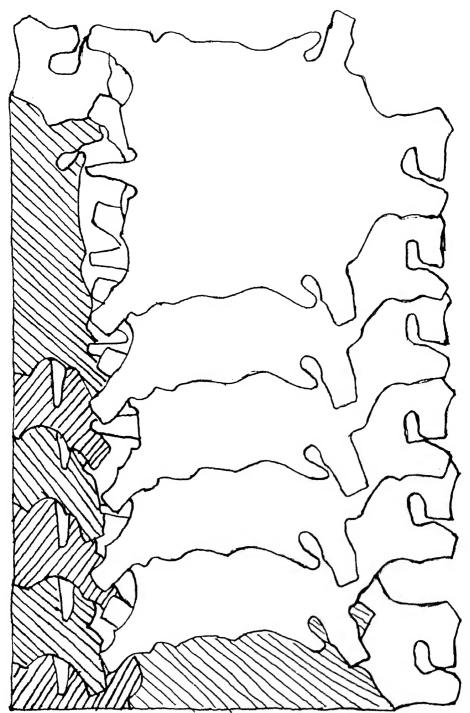


Fig. 50.

Showing How Side Edges Are Applied After Corner Hides Are in Place.

Side Edges

"With the back edge completed, the sides can be continued to the front of the pack. This consists of lapping hides along the edges from back to front, in the same manner as in the back edge. Heads are placed toward the front of the pack. The corner having been completed, it is not necessary to fold over the butt of the second side edge hide. Winter hides should be spaced approximately two feet apart progressively toward the front edge; summer hides slightly more. [See Fig. 50.] When the front of the pack is reached, the head and shoulders, or butts, are folded over, as in the back of the side edge, to start the corner of the front edge.



"The pack edges tend to provide sloping surfaces to retain brine within the pack and permit its escape slowly by percolation. With the three edges completed, the *spreads* can be put in place, to build the layer up evenly. Place the heads of the hides toward the center of the pack. The first hide should be spread flat, flesh side up, shanks about a foot from the back edge, and the butt about the same distance from the side edges and upon the flesh side of the side-edge hides. Then successive hides should be spread progressively toward the front, with about two feet separation to match the side edges and maintain the pack as level as possible. [See Fig. 51.] The spread hides are lapped as they reach the front to form the front edge. Repeat this first spread on the other side of the pack."

The Spreads

"Then the second spread is put on, with the butts of the hides placed on the side edges, tails, overhanging shanks, and tag ends lapped over and salt placed under them. [See Fig. 52]. With the second spreads applied to both sides of the pack, the center spread, completing the fill, can be put in. Heads can be turned either way so that low spots or unevenness in the other spreads can be levelled. Hides are lapped as they reach the front to complete the front edge.

"Hide spreaders grasp the hide by tail and head, flesh sides folded together, and hold both shanks in the other hand, carrying same to its position in the pack. Care must be exercised not to drag any portion of the carried hide over those already salted, so as to expose the underneath hides to decomposition or poor cure, where such dragging occurred. Each spreader drops the underneath shank and throws the other one over with one motion. The salt on the underneath hides will not be disturbed, if hides are handled in this manner.

"Salt usually is spread with a No. 8 scoop shovel, holding 30 to 35 lbs. of salt. It is applied with a sweeping motion so that every portion of the flesh side of the hide is covered uniformly throughout. A pound of clean, pure salt to a pound of hide is a safe rule to follow, or about two scoops of salt for the average hide.

"Where hides have been folded over, as in the edges, or to fill uneven places in the spreads, the hair side, which is exposed should have salt sprinkled on it before another hide is placed above it.

"With the first *layer* of hides completed, succeeding layers (edges and spreads) should be put down until the pack has reached the desired height. In some plants the last layer of edges and fill is put on much closer, so that there is a distinct slant to the hides as they approach the front edge. However, when the pack is completed, it should be level throughout its entire length. Generous quantities of salt are spread on this last layer, so that not a particle of any hide is showing. This is termed *laying-bye* the pack. This procedure will make a strong brine which will percolate through the entire pack, keeping every hide moist and in good merchantable condition."

Where there is a large and continuous flow of green hides to the hide cellar, hide packs can be built up correspondingly quickly, but in small plants, it may take as long as a month to get hides enough to build up a pack. This is undesirable because the green hides placed on top are continually losing water, which passes through the pack to the earlier hides below and upsets their proper conditioning. Better hides are obtained when a pack is built quickly. Most of the better hide cellars are kept at a uniform temperature of about 55 °F. Where the temperature is higher than this, greater shrinkages in the stock occur. Air blowing over the packs tends to cause the edges to dry out, and so drafts are avoided. After the

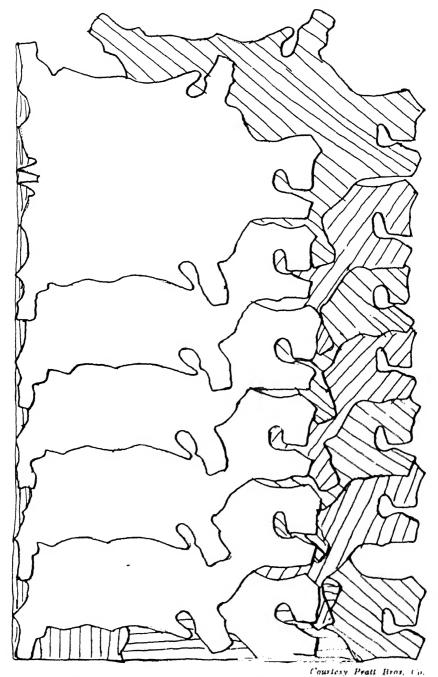


Fig. 52. How the Second Spread is Applied Closer to the Edge.

pack has been completely built, it is usually allowed to remain undisturbed for at least 30 days to effect complete curing.

Curing Action

The object of curing hides is to protect them against the putrefactive action of bacteria until the tanner is ready to start their conversion into leather. Salt does not kill bacteria, but it restricts their activity and reproduction. Wilson and Vollmar found that bacteria from a tannery soak water would not develop in a 6 per cent salt solution under otherwise ideal conditions for their growth. The primary object of the elaborate procedure described above is to saturate the water of the hides with salt so as to restrict bacterial action. Time enough must be allowed to permit the diffusion of salt to every part of the hides.

The use of one pound of salt per pound of hide represents much more salt than can be dissolved by the water of the hide, but it tends to insure a more rapid and complete diffusion of salt into every part of a hide and to produce a saturated solution. McLaughlin and Theis found that 62 per cent of the green weight of a hide consists of water. The 62 lbs. of water contained in 100 lbs. of green hide can dissolve a maximum of only about 23 lbs. of salt, leaving 77 lbs. undissolved. When the hide pack is taken down, some of the undissolved salt is recovered by shaking it off the hides, but such recovered salt should be washed before reusing to prevent the staining of hides often caused by impure salt. The washing also removes bacteria that adjust themselves to salt and become salophilic.

Shrinkage

During the curing operation, the salt causes much water to come out of the hides and to drain off as brine. This causes the loss in weight of the hides that is known as *shrinkage*. This does not represent any real loss, but it becomes very important in determining the price at which the hides can be sold. Where the shrinkage is larger, the water content of the hide is correspondingly smaller, and it is worth more per pound because it contains more leather-making material per pound. In an experiment on effects of curing, McLaughlin and Theis found that 100 lbs, of green hide, containing 62 lbs, of water, lost 35 lbs, of water and gained 6 lbs, of salt.

Effects of Delayed Curing

It is well known that bacterial action sets in very soon after the death of an animal, making it desirable to start curing as quickly as possible after the animal heat of the hide has been dissipated. McLaughlin and Theis found also that delay in starting curing causes the salt to be taken up by the hide at a very much slower rate, tending still further to favor bacterial action. First they showed that salt is absorbed 25 times as rapidly through the flesh side of the hide as through the grain side, which can readily be appreciated from the knowledge of the structure of the epidermis gained in Chapter 1. Then they found that delaying curing only one hour caused the salt to diffuse into the hide only 69 per cent as fast as when curing was started at once. A delay of 6 hours reduced this diffusion rate to only 26 per cent.

Ultimately the hides became saturated with salt, but the retardation of its diffusion into the hide permitted more time for putrefactive changes which lower the leather yield. The coagulation of blood and of coagulable proteins in the hide retard greatly the diffusion of salt into it. McLaughlin and Rockwell found that the blood left in hides not only greatly favors bacterial action, but greatly increases the amount of salt required for effective preservation.

South American Hides

Argentina is an important cattle-raising country and naturally has developed a great packing industry, which ships much frozen beef to all parts of the world. For each animal slaughtered, there is, of course, a hide, and Argentina has become noted as an enormous producer and exporter of hides. The hides from their larger packing houses are known as *Frigorifico* hides and are comparable to our *big-packer* hides. In the matter of curing, they may be considered superior to our average run of big-packer hides.

Before slaughter, the animals are washed thoroughly. After flaying, the hides are washed to remove blood and soluble protein matter and the hair is scraped under a spray of water. The flesh side is then brushed vigorously and surplus flesh is removed. They are then soaked for 48 hours in strong brine and drained, after which they are salted.

McLaughlin and Theis performed a very interesting series of experiments showing the unmistakable advantages of the Frigoritico method over that used in curing hides in this country. As each hide left the carcass, it was split down the line of the backbone into two sides. One side was salted according to the method used in this country within an hour after flaying; the other was washed at once with running water, soaked for 24 hours in a 25 per cent salt solution, drained and then salted. The treatment given left and right sides was alternated. After 6 to 8 weeks of curing, the various lots of sides were shipped to a number of different tanneries to be tanned for sole leather, the two sides of each hide going together. The brined sides produced more leather than the sides merely salted and they were thicker and firmer and had only about one tenth as many salt stains.

The loss in weight from the green state to the tannery received state was 17.86 per cent for the stock that was only salted, but 19.00 per cent for the brined stock. If no leather-forming material was lost with either cure, the brined stock, should have produced 1.014 times as much leather as the salted stock or a gain of 1.4 per cent. The actual gain was 2.0 per cent. That the gain was a real one is indicated by the fact that the brined stock gained 0.8 per cent more as finished sole leather than the salted stock based on the green weights of the sides. Because the per centage gains appear to be small, many tanners have expressed doubt as to whether they would justify the premium that would have to be paid for the brining operation. However, since some packers are brining a portion of their hides, there is a possibility that the method may ultimately be generally adopted in this country. Brining is valuable to the tanner in giving him a more uniformly cured material in addition to a gain in weight yield.

Pickling

Of the more than 49 million sheep and lamb skins made available to American tanners in 1939, nearly 22 million were of domestic production. More than 17 million animals were slaughtered in domestic packing plants under Federal inspection. Since wool is a valuable by product, many packers remove the wool from the skins before preparing the skins for the market and thus perform on them a part of the work which tanners do on the other types of hides and skins.

In some packing plants, after the flaying operation, the skins are coated on the flesh side with a paste made from lime and sodium sulfide and allowed to hang over night. The lime and sulfide diffuse through the skin to the epidermis, destroying the epithelial tissues that line the hair follicles. This loosens the wool so that it may be pulled or rubbed from the skins. The dewooled skins are then limed, bated, washed and pickled.

The pickle liquor is a solution of sulfuric acid and salt and is usually applied to the skins in a vat equipped with a paddle wheel, which agitates both liquor and stock during the pickling operation. Into a paddle vat of 2500 gals, total capacity, a solution of 2500 lbs. of salt and 200 lbs. of sulfuric acid in 1900 gals, water is run and intimately mixed. Then 5000 lbs. of bated sheep skins is dumped into the liquor with the paddle running to turn over the stock and liquor and maintain intimate contact of skins and liquor. The alkaline materials contained in the skins neutralize some of the acid and some acid combines chemically with the skin protein. The result is rapid disappearance of much of the acid. At intervals, samples of the pickle liquor are analyzed to determine how rapidly the acid is disappearing. After several hours, successive samples show no further change in composition, indicating that an equilibrium has been established between the skins and the liquor. Additions of acid and salt are made so that when equilibrium is established, the liquor will contain 1 lb. of salt and 13 oz. of sulfuric acid per gallon. The stock is then hauled out, allowed to drain and bundled for shipment. It is referred to as pickled stock.

If pickled sheepskins are kept at temperatures not exceeding 70°F., they appear to undergo no decomposition, even if kept for as long as two years. However, if they are stored in a place where the temperature may exceed 90°F., the acid tends to gelatinize the skin fibers and much harm may be done. Very much less acid than is used would effectively protect the skins against bacterial action, but would permit the growth of molds. The amount of acid used is the minimum that will protect the skins from becoming moldy. As an added protection against molds, suitable fungicides are often added to the pickle liquors.

Drying

Probably the most effective method of preserving animal skin against decomposition is to dry it. Bacteria and molds require water for their activity, and thoroughly dried skins may be kept indefinitely without danger of decomposition. However, it is not a simple matter to dry heavy hides without a considerable amount of decomposition occurring during the drying. If the hides are dried too rapidly at first, the outer surfaces become hard and dry while the fibers inside are still wet. This greatly delays the removal of the water from the inside, and putrefaction may set in before complete drying is achieved, which does not become evident until the tanner gets them and wets them back to start his operations.

If the drying is carried on too slowly, putrefaction may set in throughout the hide long before it is completely dry. In many tropical countries, the temperature and relative humidity are usually very high, and proper drying equipment is not available, making it necessary to resort to various procedures to prevent decomposition during the drying.

Where hides and skins are produced for domestic consumption, it is usually more satisfactory simply to cure them rather than to dry them, but drying is preferable in many remote countries where facilities for drying are much better than those for curing and the stock must be shipped over long distances. When hides and skins are simply dried without the addition of any salt or other material, they become very hard and stiff and so are referred to as flint hides, or flint-dried hides; sometimes merely as dried hides.

During the drying of a hide, the fibers become very firmly glued together and this presents the tanner with the serious problem of getting them soaked back properly with water without causing any damage to them. With cured hides, he has only to soak them in plain water and proceed with his operations. Dried hides

also represent more of a gamble to the tanner in his purchases because he cannot see what damages they may have until he already has them in process.

Salting and Drying

The danger of putrefaction during the drying of hides and skins can be greatly reduced by salting them before proceeding with drying. Stock of better quality is produced and the tanner has much less difficulty in soaking them back to a normal water content. Hides preserved in this way are known as *dry*, *salted* hides.

Although pure salt is plentiful and cheap in the United States, it is scarce and expensive in many other countries. Sometimes the only salt that is available for preserving hides economically is very impure and may contain salts of aluminum and other materials that have a tanning action on the hide. The salts used in some localities so affect the hides as to cause the tanner the most annoying difficulties in his various operations, particularly in getting the stock properly unhaired without damage to the stock.

Although some dried hides and skins from almost every kind of animal are imported into this country, most of the cattle hides and skins and horse hides are cured and arrive in the green, salted state and most of the sheepskins are pickled, but the vast majority of goat skins are dried or dry, salted. Being very small, goat skins lend themselves readily to drying and they are usually shipped from remote parts of the earth.

Of the more than 39 million goat skins made available to American tanners in 1939, nearly 38 million skins were imported as dried skins, many of which were salted before drying. Only a little over one million were imported in the green, salted state and only about a quarter of one million were of domestic production.

Bundling Hides and Skins for Shipment

In the big packing houses, the first operation in preparing the hides for ship ment is the pulling of the hide pack, which has been fully cured. Pulling is just the reverse of the procedure involved in building the hide pack. The first hides to come off the pack are the last ones that were put in the front edges of the center spread. The hides are then taken off progressively toward the back edge. Then the second spreads are removed, followed by the first spreads and the side and back edges of each layer. Each hide is usually taken by two men and dragged to the front of the hide pack, bringing as much loose salt with it as possible. The hide is then turned over with the hair side up so as to dump most of the excess salt onto the floor, from which it is trucked away to be reused after cleaning.

The hide is then dragged onto a wooden *horse*, which is rectangular in shape, about 4 by 7 feet, and rests on legs about two feet high. It is slatted or cross braced so as to provide a surface on which hides may be placed to shake off the adhering salt. Four men grasp the hide by the shanks and centers and raise and slap it vigorously on the horse. The hide is then turned flesh side up and drawn across a *beaver* to scrape the salt from the hair side. The beaver consists of two long, heavy planks put together in the form of an inverted V.

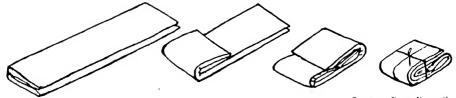
At this point, the hides are inspected and graded. It is customary for the tanner or hide buyer to have an inspector on hand to see that the hides are as represented in the sales contract. The inspection and grading will be discussed in Chapter 6.

When the hides are bundled, the purchaser may determine whether he prefers them to be rolled with the hair side in or out. In the No. 1 selections, where it is desired to protect the grain surface as much as possible, it is customary to roll the hides hair side in to protect the grain surface from damage in dragging the hide across the floor. Hides rolled with the hair side in remain in a more moist condition because the hair retains much moisture when rolled in and the stock reaches the tanner with less transit shrinkage. The No. 2 selections, which are much fewer in number in the big packing houses, are usually rolled flesh side in.



Fig. 53. Initial Steps in Folding a Hide in Bundling. The head and shoulders and one belly have been folded over and the right front and hind shanks have been laid on the folded belly portion.

Price describes the final rolling and bundling as follows: "To roll hides, the head and neck of the hide are thrown in a point even with the forelegs. Then fold in the bellies and lay the shanks upon this fold, hair to hair or flesh to flesh according to selection. [See Fig. 53.] Fold the two outside edges to the center line of the hide and then place the two folds together. The hide now is laid out in a long



Courtesy Pratt Bros. Co.

Fig. 54. Final Steps in Bundling a Hide.

strip, fifteen or eighteen inches wide. [See Fig. 54.] Throw the butt portion forward beyond the middle of the strip, then the forward part is folded over on top of this already folded butt portion, and again the butt end is doubled over to make a neat square bundle.

"Hides are usually tied with either jute or sisal strings having several plies and of about 7-ft, lengths. A bowline or hide knot, which holds its loop, is tied in onend and a running noose is made therein, which is slipped around the rolled bundle from side to side and drawn taut in the center of the bundle. The string then is looped crosswise around the folds of the bundle and securely knotted with a slip knot, so that the string may be re-used if necessary. Hide rope weighing more than ten pounds per 100 strings is frowned on by most inspectors and additional tare demanded. The bundled hides are then tested for proper weight divisions and piled, five high, to await shipment."

Dried Stock

When hides or skins are dried, they become so hard that it is impossible to fold them up into neat bundles. Goat skins are so small that they can be laid out full size into bundles of a dozen each and handled easily in shipment. Many dried sheep skins come to this country with the wool left on so that they can be tanned with the wool on for coats or for slippers. Many of these are folded over once along the line of the backbone and can then be well packed in bundles of a dozen or more each. Heavy hides may be shipped without folding at all or may be tolded once to facilitate handling.

In bundling dried sheep skins and goat skins, it is customary to pack naphthalene or other insecticides between the skins to protect them against moths and other insects.

Pickled and Green, Salted Skins

Hides and skins cured and bundled like big packer hides may be shipped in bundles like these hides, but when skins have not been fully drained in curing they are often packed in barrels or casks after bundling. The general method of bundling is the same for light skins as for big packer hides, except for the not that many small skins may be packed into a single bundle. Where pickled skins have been well drained before building, they can be shipped in buildles where the shipping distances are not great, but packing the bundles in cosks protect; them against damages and drying where they may be a long time in transit.

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Chapter 3

Domestic Production and Imports of Hides and Skins

In the commercial production of leather, it is very important to know the recognized sources of hides and skins and the quantities available, as well as the conditions in which various types of raw stock are received and price variations. The methods of purchasing raw stock and selections for specific types of leather

Table 1. Movement into Sight of Cattle Hides (in thousands of hides).

Month, 1939	Inspected slaughter	Uninspected slaughter	Imports minus exports	Total movement into sight
January	762	605	285	1,652
Pebruary	653	650	263	1,566
March	774	625	346	1,745
April	677	560	195	1,432
May	814	609	181	1,604
June	<i>77</i> 8	572	162	1,512
July	<i>7</i> 82	585	124	1,491
August	823	560	184	1,567
September	880	540	198	1,618
October	893	605	151	1,649
November	837	590	275	1,702
December	773	537	355	1,665
Totals	9,446	<i>7</i> ,038	2,719	19,203

Table 2. Movement into Sight of Kip and Calf Skins (in thousands of skins).

Month, 1939	Inspected slaughter	Uninspected slaughter	Imports minus exports	Total movement into sight
January	415	570	437	1,422
February	385	560	390	1,335
March	478	550	359	1,387
April	457	410	394	1,261
May	509	541	267	1,317
June	449	595	321	1,365
July	417	566	323	1,306
August	414	520	252	1,186
September	427	480	243	1,150
October	482	430	194	1,106
November	450	462	328	1,240
December	381	468	209	1,058
Totals	5,264	6,152	3,717	15,133

along with price variations over a period of twenty years will be dealt with separately in Chapter 6. It has been deemed sufficient for the purposes of this book to limit this chapter to an account of all the hides and skins made available to

Month, 1939	Inspected slaughter	Uninspected slaughter	Imports minus exports	Total movement into sight
January	1,456		3,546	
February	1,361		1,814	
March	1,473		1,897	
April	1,224		2,077	
May	1,392		2,304	
Tune	1,401		1,939	
Tuly	1,399		<i>2</i> ,066	
August	1,457		2,286	
September	1,635		2,307	
October	1,585		1,851	
November	1,469		3,377	
December	1,389		2,036	
Totals	17.241	4,447	27,500	49,188

Table 3. Movement into Sight of Sheep and Lamb Skins (in thousands of skins).

(Mr. Holt supplied the total figure for uninspected slaughter for the year).

Table 4. Movement into Sight of Goat and Kid Skius (in thousands of skins).

	Imports
	minus
Month, 1939	exports
January	3,570
February	3,347
March	3,878
April	3,006
May	3,746
June	3,038
July	3,036
August	2,985
September	2,315
October	3,041
November	3,081
December	3,974
Total	39,017

(Mr. Holt estimates the domestic production of goat skins in the Southwest at about 250,000 skins per year, which is insignificant compared to the more than 39 million skins imported).

American tanners in one full year. The year 1939 was selected because it is the latest year for which complete data is available at the time of writing this book.

Mr. E. G. Holt, Chief of the Leather and Rubber Division of the Bureau of Foreign and Domestic Commerce of the United States Department of Commerce very kindly supplied the advance official data for the calendar year 1939 on all imports of hides and skins, with countries of origin, numbers of pieces imported, their kinds and conditions as to whether wet or dry, and their prices. He also provided data on exports and also on the domestic slaughter of cattle, calves, sheep, hogs, goats and horses.

Mr. I. R. Glass, of the Tanners' Council of America, kindly furnished data on the movement into sight of hides and skins for the calendar year 1939 by months. By movement into sight is meant total domestic production plus imports minus exports. In other words, it means the actual quantity of stock made available to American tanners during the year.

A division is made according to whether domestic slaughter was done under

Federal inspection or uninspected. Mr. Glass' figures for cattle hides, calf and kip skins, sheep and lamb skins, and goat and kid skins are given in Tables 1 to 4, inclusive.

Table 5. Imports for Consumption of Cattle Hides for Calendar Year 1939.

		-Dry hides-				
Country	pieces	lbs.	dollars	pieces	lbs.	dollars
Argentina	198,041	3,697,088	431,342	1,695,428	73,501,023	7,060,407
Australia	11,225	252,515	23,439	42,329	1,475,699	122,759
Belgium				9,998	335,980	15,485
Bolivia	200	5.372	444			
Brazil	25,785	514,471	68,832	343,115	18,962,085	1,298,917
British East Africa		27,854	2,910	0.0,220		2,220,22
British India	93,488	1,346,719	132,470			
British South Africa		103,412	12,134	3,000	95,005	8,458
Bulgaria	•			200	8,923	2,674
Burma	1,500	20,273	1,587	400	12,202	665
Canada	28,649	485,270	58,812	499,099	23,026,717	1,773,860
China	19,796	353,658	60,348	•		1,775,000
				225	10,637	868
Colombia	2,098	46,562	6,006		. ,	
Cuba	• • • •		• • • •	5,694	232,699	23,984
Czechoslovakia	0.710	47.060	4.04.3	200	8,173	2,672
Dominican Republic	2,713	47,860	4,342	100	3,691	302
Ethiopia	350	4,815	3 9 7		011 770	10.164
Finland				5,826	211,573	19,164
France	1,000	20, 7 46	2,374	7,906	366,920	50,521
Germany				300	18,198	4,424
Guatemala	1,200	30,600	3,000		• • • •	
Honduras	1,576	2 7,7 06	3,141			• • • •
Italy				10,717	465,059	141,255
Jamaica				200	8,200	757
Madagascar	1,500	18,926	1,77 8		• • • •	
Mexico				61,231	2,324,331	191,667
Netherlands	201	5,778	258	1,720	52,365	5,100
Newfoundland & Lal	b			5,529	208,320	14,619
New Zealand				79,395	2,939,539	259,078
Nicaragua	557	12,235	1,328			
Nigeria	2,080	26,558	2,689			
Norway				8,750	311,413	26,930
Palestine	100	2,290	184	1,000	26,858	1,661
Peru	5,612	138,796	17,242	3	179	21
Philippine Islands				5,566	172,195	11,196
Poland & Danzig				1,988	90,250	8,768
Sweden				7,713	311,343	29,852
Switzerland				5,218	402,301	84,935
Union of So. Africa	12,750	239,176	26,791	3,642	169,675	14,290
United Kingdom	1,033	14,003	1,493	1,865	76,959	7,170
Uruguay	780	10,156	1,155	17,000	782,441	73,947
Venezuela	1,915	43,429	3,569	17,000	/ (/m ₁ TTL	11,271
v Chezhent	1,713	7.7.729	0,000	• • • •	• • • •	
Totals	421,199	7,496,268	868,125	2,825,357	126,610,953	11,256,406
		. , ,		, ,	, , , , , , , , , , , , , , , , , , , ,	,

During 1939, 66,003,000 hogs were slaughtered in the United States. Because of the American practice of leaving the skin on the meat, only a very small percentage of the skins became available to tanners. A large number of skin strips

from over the lard areas of the hogs was produced by the larger packers, but no reliable figures appear to be available as to the exact number. Such whole skins as were produced were chiefly of country take off and of rather low quality. The best hog skins were imported, but no reliable figures are available as to quantity because of the practice of listing importations of hog skins under the vague classification of "other hides and skins."

Horse meat is not generally relished in the United States and so most of the domestic horse hides come from animals that have died in service, and probably only about one-third of the hides are recovered and used for tanning. Actual data

Table 6. Imports for Consumption of Cattle Kips for Calendar Year 1939.

		Dry kips		,	Wet kips	
Country	pieces	lbs.	dollars	pieces	Hest.	dollars
Argentina	152,622	1,610,226	184,842	38,313	664,650	85,454
Australia	2,123	25,472	2,270	2,583	38,172	3,260
Belgium				3,000	30,450	6,984
Brazil	30	304	145	6,505	120,772	5,462
British East Africa	10,080	87,724	8,858			
British India	53,400	514,921	65,360			
Burma	3,000	24,509	3,002			
Canada	186	1,524	123	113,685	2,000,382	225,425
China	720	8,402	1,495			
Colombia	37	224	25	550	13,291	1,401
Cuba				2,105	37,656	2,587
Czechoslovakia				5,000	63,316	11,306
Denmark				5,100	03,651	11,655
Dominican Republic				1,220	24,312	2,182
France	• • • •	• • • •		77,912	1,154,977	225,435
Mexico		• • • •		1,314	30,985	2,164
Netherland India	1,287	12,121	4,371			
Netherlands		,	****	2,100	29,157	4.438
New Zealand				2,858	60,079	0.817
Norway	3,000	20,823	2,989		1 7 7 7	1.131.14.4
Nicaragua				22	367	3.3
P'eru	200	1,773	266	1 1 1 1	1111	111
Philippine Islands		*,,,,,		1,500	34,540	2,159
Sweden				54,710	777,034	125,750
Switzerland				16,755	293,913	54.83.2
Union of South Africa	7,000	50,755	7.228	*		
United Kingdom	•	•		E 100	111721	11 7411
	• • • •	* * * *		5,100	112,732	8,348
Uruguay			4 . 4 .	6,000	123,524	27,869
Yugoslavia	(11)	(al)(a	87	8,330	104,490	18,753
Totals	233,745	2,359,384	281,061	354,662	5,784,456	832,298

are unobtainable, but Mr. Holt estimates that out of a total horse mortality of from 1,600,000 to 2,400,000 animals per year, only from 5,35,000 to 8,00,000 hides are recovered. Many of these are of doubtful quality, the best hides being imported.

Of the 19,203,000 cattle hides made available to American tanners in 1939, 85,8 per cent were of domestic production and only 14.2 per cent were imported; of the 15,133,000 kip and calf skins, 75,4 per cent were of domestic production and only 24.6 per cent were imported; of the 49,188,000 sheep and lamb skins, 44.1 per cent were of domestic production and 55,9 per cent imported; but of the more than 39,000,000 goat and kid skins, more than 99 per cent were imported. No reliable

figures could be obtained for the domestic production of other kinds of hides and skins.

Mr. Holt has provided complete data on imports for consumption of hides and skins for the calendar year 1939; these are given in Tables 5 to 18, inclusive.

During 1939, there were exported 526,869 cattle hides, 25,451 kip skins, 170,666 calf skins, 1,229,631 goat and sheep skins, listed together, and 5,309,334 lbs. of raw stock listed under the general heading "other hides and skins."

Table 7. Imports for Consumption of Calf Skins for Calendar Year 1939.

Country	pieces	-Dry skins- lbs.	dollars	pieces	-Wet skins- lbs,	dollars
Argentina	35,512	175,410	20,728	10,144	117,626	12,717
Australia	25,352	81,588	9,897	301,386	1,504,980	244,315
Barbados	1,763	3,215	404		1,001,200	211,020
Belgium		••••		7,000	80,454	15,182
Bolivia	45	87	68	7,000	00,101	10,102
Brazil	4,335	13,103	2,263			
British East Africa	135,500	288,875	32,045	2,400	5,573	599
British India	31,550	98,837	11,548		0,070	
Canada	11,356	52,855	8,542	327,157	2,436,412	298,132
China	3,980	7,957	1,886	()27,107	2,100,112	250,202
Colombia	320	1,669	211			
Denmark	1,269	6,614	797	1,000	10,582	1,549
Estonia	22,650	51,930	23,508	48,250	258,321	50,729
Ethiopia	18,600	44,486	4,688			
Finland	88,800	189,270	74,922	75,070	480,546	76,859
France		••••	,	367,538	3,738,556	775,306
Germany	15,000	54,895	16,319	3,480	27,762	6,204
Honduras	30	82	16		••••	
Latvia	51,340	118,800	50,860	147,504	793,467	154,259
Lithuania	43,557	103,018	40,547	45,644	248,560	42,400
Mexico		•		1,137	7,594	709
Netherlands	113,479	364,467	113,838	21,000	98,765	14,013
Newfoundland & Lab.				1,500	10,500	840
New Zealand	40,484	182,454	41,806	559,724	2,578,604	522,889
Norway	67,351	168,899	64,691	82,951	544,243	91,186
Poland & Danzig	126,928	251,172	113,748	170,402	998,305	175,697
Saudi Arabia	47,690	112,568	11,769			
Sweden				58,246	546,580	71,303
Switzerland				16,716	179,424	41,460
Thailand				1,100	12,466	655
Union of So. Africa	36,130	145,724	17,683	1,992	10,724	1,404
United Kingdom	32	90	34	97,048	892,127	165,272
Uruguay	27,000	95,43 <i>7</i>	18,733			
Yugoslavia	4,392	21,962	5,560	21,279	216,989	48,026
Totals	945,445	2,635,464	687,111	2,369,668	15,799,160	2,811,705

Tanners desiring more detailed information than is given in the tables should consult the trade commissioners on the various countries and brokers who specialize in raw stock from foreign countries. The tables are valuable in indicating the countries of origin, kinds and amounts of stock, average weights and dollar values. Wet stock usually refers to the green, salted state and pickled stock to the pickled and drained state. Dry stock has a weight roughly one-half of that of its equivalent in the green, salted state.

Table 8. Imports for Consumption of Goat and Kid Skins for Calendar Year 1939.

Country	pieces	——Dry skins— lbs.	dollars	pieces	-Wet skins- lbs.	dollars
Aden	115,350		32,330			Contain
Algeria	614,578	1,113,781	224,792			
Argentina	2,505,238	4,540,665	1,010,588			
Barbados	12,694		2,010,300	• • • • •	• • • •	
Belgium	35,114	10,739 51,169	2,971	70 075	F2 F60	43.323
Bolivia	1,978	21,109	21,655	78,975	53,569	42,232
Brazil	4,929,245	3,172	720		• • • •	
British East Africa	1 407 105	5,869,222	1,854,326	• • • •	• • • •	
British India	10,999,461	1,604,801	486,451	1 01 2 0 40	0.000	4.111
	10,888,461	22,823,030	4,121,716	1,013,940	2,806,433	362,661
*British West Indies Bulgaria		18,768	4,873			
Canada	62,700	63,047	28,853			
Chile	8,050	14,137	4,770			
	49,900	117,952	21,101			
China	1,951,189	3,680,175	893,581			
Colombia	272,850	508,051	88,658			
Czechoslovakia	28,020	73,892	24,038	6,400	4,273	3,399
Dominican Republic		284,650	62,676			
Ecuador	7,748	14,093	2,747	* * * *		
Egypt	158,050	232,160	45,324			
Ethiopia	629,891	724,147	194,935			
France	98,014	110,024	52,941	6,063	3,0.27	3,179
*French Africa	48,823	58,208	12,101			
French West Indies	1,089	1,154	229			
Germany	64,623	68 , 567	35,945	20,583	19,269	10,001
Haiti, Republic of	373,395	401,051	82,153			
Honduras	24	40	8		* * * * *	
Iran (Persia)	300,632	868,335	119,840			
Iraq	162,597	411,816	58,452			
Irish Free State	5,702	48,040	1,689		* 1 * 4	
Italian Africa	351,668	355,676	80,453			
Italy	93,693	119,938	38,817	9,966	4,011	4.173
Jamaica	139,892	205,150	63,823			
Mexico	1,332,775	2,421,105	634,395			1 1
Morocco	482,097	1,018,737	160,869			
Netherland India	1,841,287	1,477,708	665,332		4423	
Netherlands	21,198	64,652	27,784			
Netherland W. Indies		82,389	16,646			
Nigeria	3,459,560	3,519,221	1,649,793			
Norway	7,600	15,260	8,737	****		
Palestine Peru	68,965	179,789	27,314	120 =	202	54
	693,539	1,197,319	335,978			11/1
Poland & Danzig	5,769	8,930	3,090	4 1 1 2		
Portugal	270,976	419,551	156,768			
*Portuguese Africa	1,101	4,518	657		4 1 5 4	
Rumania	96,738	118,687	37,741			
Saudi Arabia Spain	1,122,206	1,372,544	264,759			
Switzerland	60,295	66,423	31,683	****		
Switzerland	46,268	46,678	25,042			
Syria Tunisia	245,171	672,234	118,820			
	72,702	148,774	29,451			
Turkey	467,368	1,480,080	242,040			
Union of So. Africa Venezuela	1,014,959	2,694,087	505,722			
	701,252	1,319,928	276,220		***	* * * *
Yugoslavia	170,459	313,444	76,752		F 3 + 3	2111
Totals 33	7 001 626	(21010-1				
	7,881,635	63,124,036	14,969,149	1,136,047	2,890,874	425,699

Indicates countries other than those named.

Table 9. Imports for Consumption of Sheep and Lamb Skins for Calendar Year 1939.

Country	Dieces	—Dry slats— lbs.	dollars	Dry	and green and lbs.	wooled
Aden	56,660	132,656	25,986	•		
Argentina	68,920	115,261	23,277	238,428	772,512	116,090
Australia	84,205	107,104	8,796	544,420	2,750,949	330,594
Barbados	13,521	16,311	2,809			
Belgium	5,342	5,522	2,738			
Brazil	635,393	984.865	256.018	930,126	1,103,640	338,277
British East Africa	293,837	510,475	143,890		2,200,010	000,277
British India	34,196	54,697	13,317	• • • • •	••••	••••
British West Indies	10,694	14,385	2,377	••••		••••
Bulgaria	300	562	187	• • • • •		••••
Canada	42,666	98.212	10,726	5,341	18.344	1.691
Chile	2,944	5,919	891	512,704	1,714,137	196,734
Colombia	3,000	5,936	841	•		•
Ecuador	•	2,230		1,903	3,962	658
Egypt	196,827	822,854	112,725	,	•	030
Ethiopia	25,200	47,065	7,148	• • • • •		••••
Falkland Islands	•	•	7,140	694	2.149	352
Finland	• • • •	• • • •	• • • •	200	947	153
France	78,678	98,836	8,845		247	155
French West Indies	651	981	134	• • • •	••••	• • • • •
	31	59	40	• • • • •	••••	••••
Haiti, Republic of	6.745	30.800	3.091	• • • •	••••	
Iran (Persia)		1.464	674	1.000	2.000	431
Iraq	1,413			1,000	2,000	451
Italy	8,310	15,025	2,032	• • • •	• • • • •	••••
Jamaica	1,250	3,185 1,132	928 228	• • • •	• • • •	
Morocco	560			• • • •		
Netherland India	49,960	48,529	17,900	• • • •	• • • •	• • • • •
Netherland West Indies		2,045	267	• • • •	• • • •	• • • •
Nigeria	650,983	1,131,361	354,626	• • • •		• • • •
Newfoundland & Lab.	2,900	5,800	725	725 710	2 217 520	246.000
New Zealand	43,830	55,750	14,350	725,719	2,317,520	346,008
Norway	44	108	45	• • • •	• • • •	••••
Peru	104,870	105,028	13,007	0.000	2100	
Saudi Arabia	298,784	702,184	113,101	2,295	3,188	523
Union of S. Africa	355,967	1,059,715	232,217	1,006,585	2,584,930	594,985
United Kingdom	16,404	29,989	6,641	05.052	220011	00.454
Uruguay	****	****		85,024	229,214	36,474
<u>Venezuela</u>	100	200	20		;;	****
Yugoslavia	• • • •			33	66	30
Totals	3,096,573	6,214,015	1,380,597	4,054,472	11,503,558	1,963,000

^{*} Indicates countries other than those named.

Table 10. Imports for Consumption of Sheep and Lamb Skins for Calendar Year 1939.

	Pickled-	skins, fleshers and	l skivers
Country	pieces	lbs.	dollars
Argentina	4,825,633	11,374,658	1,687,530
Australia	1,485,371	3,088,382	420,846
Belgium	840	1,590	658
British India	864	2,288	288
Canada	644,144	1,558,411	216,002
Czechoslovakia	400	26.1	207
Egypt	16,375	37.465	8,936
France	66,152	107,679	44,471
Germany	200	400	119
Greece	1,200	1,091	720
Iceland	5,628	21,144	2,414
Iran (Persia)	6.138	15,607	2,066
Iraq	1,422	3,649	515
Italy	13,737	15,644	6,020
Morocco	8,304	14,776	3,248
New Zealand	12,750,327	27,054,449	3,753,863
Palestine	636	1,908	207
Spain	240	480	178
Sweden	7.872	17.510	6.156
Turkey	129,104	281,439	83,619
Union of South Africa	27,585	44,113	2,587
United Kingdom	1,211,221	1,690,358	239,084
Uruguay	374,672	724,861	81,030
Totals	21,578,065	46,058,166	6,564,764

Table II. Imports for Consumption of Buffalo Hides for Calendar Year 1939.

	e	Div and wet Buffalo hides		- 10	The antwet	le s
'ountry	picers	Hrs.	dollar.	100 m	llan.	dollas
Belgium British India	45 57,050	1,460 677,919	183 77,630	17,808	287,174	47,56,5
British Malaya				32,134	5.38,9.31	Itu, tuar
liina Egypt	2,743 3,250	99,851 14,394	11,687 4,081	1,400	51,741	5,638
Netherland India	11,729	181,429	26,126	4,087	75,889	14,988
Vetherlands			,	10,203	176 443	31 14.4
Philippine Islands Sweden	1,830 1,500	126,717 17,458	6,742 2,791	75	1,854	250
hailand	349	13,326	884			
Inited Kingdom	2,000	30,177	7,245	5,719	95,9.11	PERMIT
otals	80.496	1,162,531	137,369	71.426	1.29.301	235 420

Table 12. Imports for Consumption of Horse, Colt and Ass Hides for Calender Year 1939.

	CDry I	rides	Wet	
Country	lbs.	dollars	lbs.	dollars
Algeria			49,114	2,546
Argentina	1,661,702	155,823	5,259,036	215,401
Australia			424,462	12,954
Belgium			1.997,796	133,421
Brazil			55,666	3,560
Canada	114,634	7.146	3,964,861	204,832
Denmark			107,500	7,511
France	119,521	9.055	6.052,799	429,021
Irish Free State			21.004	1,521
Netherlands			1,727,489	168,230
Newfoundland and Labrador			1,680	50
New Zealand			86,086	2,660
Sweden			245,797	22,054
Switzerland			48,675	3,240
Tunisia			17,030	899
United Kingdom			2,583,840	175,647
The state of the s	• • • •	••••	, ,	•
Totals	1,895,857	172,024	22,642,835	1,383,547

Table 13. Imports for Consumption of Deer, Elk and Reptile Skins for Calendar Year 1939.

			-		
		eer and Elk ski		-Reptile	
Country	pieces	lbs.	dollars	pieces	dollars
Argentina	1,691	3,949	1,312	26,714	4,352
Australia	31,270	149,951	32,320	••••	**::
Bolivia	1,969	5,518	1,969	21	15
Brazil	30 7,7 36	1,049,298	389,665	71,271	7,946
British Honduras				3,459	5,269
British India				38,000	5,633
British Malaya			,	602	1,038
Canada	4,677	45,556	6,480		
China	303,165	471,212	155,749		
Colombia	6,111	10,344	2,688	4,156	7,351
Costa Rica	1,612	3,522	476	1,504	2,840
Ecuador	2,164	5,077	938	1,611	3,165
French Indo-China	17,245	110,680	8,174	3,125	835
French Oceania	37,009	154,560	30,517		
Germany	659	2,919	590		
Guatemala	4,100	9,800	1,960	35	63
Honduras	14,612	27,880	4,676	8,699	15,897
Hong Kong					222
Jamaica				70	70
Mexico				65,631	134,090
Netherland India	7,450	26,148	2,968	96,932	34,152
New Zealand	29,353	98,460	39,772		
Nicaragua	69,855	140,300	24,209	6,174	18,671
Norway	10	529	70		
Panama	214	429	43	1,162	928
Peru	23,630	67,943	29,320		
Philippine Islands				14,514	3,858
*Portuguese Africa				1,907	9,125
Salvador -	696	1,393	300	1,185	1,651
Sweden	10	550	65		
Thailand	34,088	89,034	12,563		
United Kingdom	10,252	50.750	9,250		
Uruguay	1,122	5,291	927		
Venezuela	9,054	21,076	2,152	5,560	17,243
Totals	919,754	2,552,169	759,153	352,332	274,414

Table 14. Imports for Consumption of Kangaroo and Wallaby Skins for Calendar Year 1939.

Country	pieces	lbs.	dollars
Australia	939,434	1,050,052	588,012

Table 15. Imports for Consumption of Shark Skins for Calendar Year 1939.

Country	lbs.	dollars
Brazil	227	90
British Honduras	3,554	4.14
*British West Indies	90,082	9.919
Cuba	122,317	14,021
Colombia	220	50
Costa Rica	610	68
Honduras	2,331	350
Tamaica	43,586	5,054
Mexico	207,165	22,202
Nicaragua	1.149	228
Portugal	1.799	767
Venezuela	36,962	6,688
Totals	510.002	59,971

^{*} Indicates countries other than those named.

Table 16. Imports for Consumption of Other Fish Skins for Calendar Year 1939,

Country Canada Mexico Newfoundland and Labrador	16s. 917,727 2,000 27,725	dollar 16,510 230 605	
Portugal	176	92	
Totals	947.628	17.437	

Table 17. Imports for Consumption of Scal Skins (not fur) for Calendar Year 1939.

Country	Han,	thellat n
Argentina	574,229	34,247
British South Africa	7,676	384
Canada	39,858	5,890
Newfoundland and Labrador	19,873	1,810
Norway	317,869	29,530
Peru	19,800	1,4.25
Totals	979,305	73:292

Table 18. Imports for Consumption of Other Hides and Skins for Calendar Year 1939.

Country	pieces	dollars
Argentina	110,095	136,554
Australia	3,181	1,983
Belgian Congo	20,700	3,895
Bolivia	14,371	13,134
Brazil	992,074	910,063
British East Africa	2,288	3,575
Canada	30,722	
China	1,000	16,632 594
Colombia		
Denmark	17,627 500	20,681
Ecuador		725
France	6,525	4,972
	6,983	8,377
French Africa	200	197
Honduras	1,018	554
Mexico	12,243	4,930
Nicaragua	3,868	1,772
Paraguay	3,000	4,348
Peru	104,838	111,868
Tunisia	5	11
Union of South Africa	3,075	18,1 3 3
United Kingdom	963	1,456
Uruguay	14,888	20,019
Venezuela	100	66
Yugoslavia	19,096	41,327
Totals	1,369,360	1,325,866

Indicates countries other than those named.

Chapter 4

Government Regulations on Imported Hides and Skins

In order to import hides and skins into the United States, two Government requirements must be met. The first is that duties must be paid in accordance with the Tariff Act of 1930 (Public Law No. 361) and the changes in import duties made since the passage of the Tariff Act of 1930. The second is that all importations shall be subject to the regulations of the Bureau of Animal Industry issued for the purpose of preventing the introduction from foreign countries into the United States of communicable diseases of livestock.

The eight paragraphs of the Tariff Act of 1930 pertaining to hides and skins are given below along with the duty charged, where dutiable. Since these paragraphs include tanned hides and skins as well as raw stock, they are kept together here for convenience.

Dutiable List

Par. 1519. (a) Dressed furs and dressed fur skins (except silver or black fox), and plates, mats, linings, strips, and crosses of dressed dog, good, or kid skins, 25 per

centum ad valorem; all the foregoing, if dyed, 30 per centum ad valorem.

(b) Manufactures of fur (except silver or black tox), turther advanced than dressing, prepared for use as material (whether or not joined or sewed together) including plates, mats, linings, strips, and crosses (except plates, mats, linings, strips, and crosses of dog, goat, and kid skins), if not dyed, 35 per centum ad valorem; it dyed, 40 per centum ad valorem.

(c) Silver or black fox furs or skins, dressed or undressed, not specially provided

for, 50 per centum ad valorem.

(d) Articles of wearing appared of every description, wholly or partly manufactured, composed wholly or in chief value of hides or skins of eattle of the bovine species, and not specially provided for, 15 per centum ad valorem; composed wholly or in chief value of dog, goat, or kid skins, and not specially provided for, 35 per centum ad valorem.

(e) Articles, wholly or partly manufactured (including for collars, for cutts, and for trimmings), wholly or in chief value of for, not specially provided for, 50 per centum

ad valorem.

Par. 1520. Hatters' furs, or furs not on the skin, prepared for hatters' use, including

fur skins carroted, 35 per centum ad valorem.

PAR. 1530. (a) Hides and skins of cattle of the hoving species (except Index and skins of the India water buffalo imported to be used in the manufacture of rawhide articles), raw or uncured, or dried, salted, or pickled, 10 per centum ad valorem.

(b) Leather (except leather provided for in subparagraph (d) of this paragraph),

made from hides or skins of cattle of the bovine species;

(1) Sole or belting leather (including offal), rough, partly finished, finished, curried, or cut or wholly or partly manufactured into outer or inner soles, blocks, strips, counters, taps, box toes, or any forms or shapes suitable for conversion into boots, shoes, footwear, or belting, 12½ per centum ad valorem;

(2) leather welting, 124 per centum ad valorem;

- (3) leather to be used in the manufacture of harness or saddlery, 1.25 per centum ad valorem;
- (4) side upper leather (including grains and splits), patent leather, and leather made from calf or kip skins, rough, partly finished, or finished, or cut or wholly

or partly manufactured into uppers, vamps, or any forms or shapes suitable for conversion into boots, shoes, or footwear, 15 per centum ad valorem;

(5) upholstery, collar, bag, case, glove, garment, or strap leather, in the rough, in the white, crust, or russet, partly finished, or finished, 20 per centum ad valorem; (6) leather to be used in the manufacture of footballs, basket balls, soccer balls,

or medicine balls, 20 per centum ad valorem;

(7) all other, rough, partly finished, finished, or curried, not specially provided

for, 15 per centum ad valorem.

(c) Leather (except leather provided for in subparagraph (d) of this paragraph), made from hides or skins of animals (including fish, reptiles, and birds, but not including cattle of the bovine species), in the rough, in the white, crust, or russet, partly finished, or finished, 25 per centum ad valorem; vegetable-tumed rough leather made from goat or sheep skins (including those commercially known as India-tanned goat or sheep skins), 10 per centum ad valorem; any of the foregoing if imported to be used in the manufacture of boots, shoes, or footwear, or cut or wholly or partly manufactured into uppers, vamps, or any forms or shapes suitable for conversion into boots, shoes, or footwear, 10 per centum ad valorem.

(d) Leather of all kinds, grained, printed, embossed, ornamented, or decorated, in any manner or to any extent (including leather finished in gold, silver, aluminum, or like effects), or by any other process (in addition to tanning) made into fancy leather, and any of the foregoing cut or wholly or partly manufactured into uppers, vamps, or any forms or shapes suitable for conversion into boots, shoes, or footwear, all the foregoing by whatever name known, and to whatever use applied, 30 per centum ad valorem.

(e) Boots, shoes, or other footwear (including athletic or sporting boots and shoes), made wholly or in chief value of leather, not specially provided for, 20 per centum ad valorem; boots, shoes, or other footwear (including athletic or sporting boots and shoes), the uppers of which are composed wholly or in chief value of wool, cotton, ramie, animal hair, fiber, rayon or other synthetic textile, silk, or substitutes for any of the foregoing, whether or not the soles are composed of leather, wood, or other materials, 35 per centum ad valorem.

(f) Harness valued at more than \$70 per set, single harness valued at more than \$40, saddles valued at more than \$40 each, saddlery, and parts (except metal parts) for any of the foregoing, 35 per centum ad valorem; saddles made wholly or in part of pigskin or imitation pigskin, 35 per centum ad valorem; saddles and harness, not specially provided for, parts thereof, except metal parts, and leather shoe laces, finished or unfinished, 15 per centum ad valorem.

(g) The Secretary of the Treasury shall prescribe methods and regulations for

carrying out the provisions of this paragraph.

Free List

Par. 1678. Fishskins, raw or salted.

Par. 1681. Furs and fur skins, not specially provided for, undressed.

Par. 1683. Goldbeaters' molds and goldbeaters' skins.

Par. 1691. Hides and skins of the India water buffalo imported to be used in the manufacture of rawhide articles.

Par. 1765. Skins of all kinds, raw, and hides not specially provided for.

Changes in Import Duties and Trade Agreements

The so called flexible tariff rate adjustment provision of the Tariff Act of 1930 is contained in Section 336, given below.

SEC. 336. EOUALIZATION OF COSTS OF PRODUCTION.

(a) Change of Classification or Duties. In order to put into force and effect the policy of Congress by this Act intended, the commission (1) upon request of the President, or (2) upon resolution of either or both Houses of Congress, or (3) upon its own motion, or (4) when in the judgment of the commission there is good and sufficient reason therefor, upon application of any interested party, shall investigate the differences in the costs of production of any domestic article and of any like or similar foreign article. In the course of the investigation the commission shall hold hearings and give reasonable public notice thereof, and shall afford reasonable opportunity for parties interested to be present, to produce evidence, and to be heard at such hearings. The commission is authorized to adopt such reasonable procedure and rules and regulations as it

deems necessary to execute its functions under this section. The commission shall report to the President the results of the investigation and its findings with respect to such differences in costs of production. If the commission finds it shown by the investigation that the duties expressly fixed by statute do not equalize the differences in the costs of production of the domestic article and the like or similar foreign article when produced in the principal competing country, the commission shall specify in its report such increases or decreases in rates of duty expressly fixed by statute (including any necessary change in classification) as it finds shown by the investigation to be necessary to equalize such differences. In no case shall the total increase or decrease of such rates of duty exceed 50 per centum of the rates expressly fixed by statute.

(b) CHANGE TO AMERICAN SELLING PRICE.—If the commission finds upon any such investigation that such differences can not be equalized by proceeding as hereinbefore provided, it shall so state in its report to the President and shall specify therein such ad valorem rates of duty based upon the American selling price (as defined in section 402 (g)) of the domestic article, as it finds shown by the investigation to be necessary to equalize such differences. In no case shall the total decrease of such rates of duty exceed

50 per centum of the rates expressly fixed by statute, and no such rate shall be increased.

(c) Proclamation by the President—The President shall by proclamation approve the rates of duty and changes in classification and in basis of value specified in any report of the commission under this section, if in his judgment such rates of duty and changes are shown by such investigation of the commission to be necessary to equalize such differences in costs of production.

(d) Effective Date of Rates and Changes,-Commencing thirty days after the date of any presidential proclamation of approval the increased or decreased rates of duty and changes in classification or in basis of value specified in the report of the commission shall take effect.

(e) Ascertainment of Differences in Costs of Production.—In ascertaining under this section the differences in costs of production, the commission shall take into

consideration, in so far as it finds it practicable:

(1) In the Case of a Domestic Article.—(A) The cost of production as hereinafter in this section defined; (B) transportation costs and other costs incident to delivery to the principal market or markets of the United States for the article; and (C) other relevant factors that constitute an advantage or disadvantage

in competition.

(2) In the Case of a Foreign Article.—(A) The cost of production as hereinafter in this section defined, or, if the commission finds that such cost is not readily ascertainable, the commission may accept as evidence thereof, or as supplemental thereto, the weighted average of the invoice prices or values for a representative period and/or the average wholesale selling price for a representative period (which price shall be that at which the article is freely offered for sale to all purchasers in the principal market or markets of the principal competing country or countries in the ordinary course of trade and in the usual wholesale quantities in such market or markets); (B) transportation costs and other costs incident to delivery to the principal market or markets of the United States for the article; (C) other relevant factors that constitute an advantage or disadvantage in competition, including advantages granted to the foreign producers by a government, person, partnership, corporation, or association in a foreign country.

(f) Modification of Changes in Duty.—Any increased or decreased rate of duty or change in classification or in basis of value which has taken effect as above provided may be modified or terminated in the same manner and subject to the same conditions and limitations (including time of taking effect) as is provided in this section in the

case of original increases, decreases, or changes.

(g) Prohibition Against Transfers from the Free List to the Dutlable List OR FROM THE DUTIABLE LIST TO THE FREE LIST.-Nothing in this section shall be construed to authorize a transfer of an article from the dutiable list to the free list or from the free list to the dutiable list, nor a change in form of duty. Whenever it is provided in any paragraph of Title I of this Act, or in any amendatory Act, that the duty or duties shall not exceed a specified ad valorem rate upon the articles provided for in such paragraph, no rate determined under the provisions of this section upon such articles shall exceed the maximum ad valorem rate so specified.

(h) Definitions.—For the purpose of this section—
(1) The term "domestic article" means an article wholly or in part the growth or product of the United States; and the term "foreign article" means an article wholly or in part the growth or product of a foreign country.

(2) The term "United States" includes the several States and Territories and the District of Columbia.

(3) The term "foreign country" means any empire, country, dominion, colony, or protectorate, or any subdivision or subdivisions thereof (other than the United

States and its possessions).

- (4) The term "cost of production", when applied with respect to either a domestic article or a foreign article, includes, for a period which is representative of conditions in production of the article: (A) The price or cost of materials, labor costs, and other direct charges incurred in the production of the article and in the processes or methods employed in its production; (B) the usual general expenses, including charges for depreciation or depletion which are representative of the equipment and property employed in the production of the article and charges for rent or interest which are representative of the cost of obtaining capital or instruments of production; and (C) the cost of containers and coverings of whatever nature, and other costs, charges, and expenses incident to placing the article in condition packed ready for delivery.
- (i) RULES AND REGULATIONS OF PRESIDENT.—The President is authorized to make all needful rules and regulations for carrying out his functions under the provisions of this section.
- (j) Rules and Regulations of Secretary of Treasury.—The Secretary of the Treasury is authorized to make such rules and regulations as he may deem necessary for the entry and declaration of foreign articles of the class or kind of articles with respect to which a change in basis of value has been made under the provisions of subdivision (b) of this section, and for the form of invoice required at time of entry.
- (k) INVESTIGATIONS PRIOR TO ENACTMENT OF ACT.—All uncompleted investigations instituted prior to the approval of this Act under the provisions of section 315 of the Tariff Act of 1922, including investigations in which the President has not proclaimed changes in classification or in basis of value or increases or decreases in rates of duty, shall be dismissed without prejudice; but the information and evidence secured by the commission in any such investigation may be given due consideration in any investigation instituted under the provisions of this section.

Further changes in tariff rates since the Tariff Act of 1930 were made possible by the Trade Agreements Act of June 12, 1934 and trade agreements have already been concluded with the countries named below.

Country	Kiffor	tive date	Treasury Decisions
			47600
Belgium	May	1, 1935	4. 4
Brazil	Jan.	1, 1936	48034
Canada	Jan.	1, 1936	48033
Canada	lan.	1, 1939	49752
Colombia	May	20, 1936	48258
Costa Rica	Aug.	2, 1937	49072
Cuba	Sept.	3, 1934	47232
		16, 1938	49458
Czechoslovakia	Apr.		
El Salvador	May	31, 1937	48947
Ecuador	Oct.	23, 1938	49710
Finland	Nov.	2, 1936	48554
France, and its colonies, dependencies, and protec-		·	
torates other than Morocco	Tune	15, 1936	48316
Guatemala	Tune	15, 1936	48317
Haiti	June	3, 1935	47667
	Mar.	2, 1936	48131
Honduras	war.	2, 1930	40131
Netherlands, including Netherland India, Nether-	** *		40000
land Guiana, and Netherland West Indian Islands	Feb.	1, 1936	48075
Nicaragua 1	Oct.	1, 1936	48511
Sweden	Aug.	5, 1935	47785
Switzerland	Feb.	15, 1936	48093
United Kingdom	Tan.	1. 1939	49753
Duty concessions terminated on March 10, 1038	J 2444	-,	

¹ Duty concessions terminated on March 10, 1938.

The United States Tariff Commission has published a list of the changes in import duties since the passage of the Tariff Act of 1930 and items on which rates

Dutiable List

Effective date and basis of change	Jan. 1, 1939; United Kingdom (T. D. 49753).) Jan. 1, 1939; Canada (T. D. 40752)	May 1, 1935; Belgium (T. D. 47600).	Jan. 1, 1939; United Kingdom (T. D. 49753).	Jan. 1, 1939; United Kingdom (T. D. 49753). [Jan. 1, 1936; Canada	Jan. 1, 1939; Canada (T. D. 49752). Jan. 1, 1939; United Kingdom (T. D.	. (52.33)
Modified rate	15% ad val	20% ad val $37\frac{1}{2}\%$ ad val	27½% ad val	10% ad val	10% ad val	l0% ad val	
Rate changed	25% ad val	30% ad val 50% ad val	35% ad val	12½% ad val	12 <u>4</u> % ad val	12 <u>‡</u> % ad val	
. Articles		All the foregoing, if dyed	田口	(1) Solo or belting feather (including offal), rough, partly finished, finished, curried, or cut or wholly or partly manufactured into outer or inner soles, blocks, strips, counters, taps, box toes, or any forms or shapes suitable for conversion into boxts, sinces, footwest, or helting.	(2) Leather welting	(3) Leather to be used in the manufacture of harness or saddlery.	(4) Side upper leather (including grains and splits), and lining leather made from calf or kip skins, rough, partly finished, or finished, or cut or wholly or partly manufactured into uppers, vamps, or any forms or shapes suitable for conversion into boots, shoes, or footwear (not including patent leather or calf or kip leather other than lining leather):
Par. No.	.519 (a)	(519 (c)	520 530 (b)				ï

Jan. 1, 1939; United Kingdom (T. D. 49753).	Jan. 1, 1939; United King-	Jan. 1, 1936; Canada (T. D. 48033)	Jan. 1, 1939; Canada (T. D. 49752).	Jan. 1, 1939; United Kingdom (T. D. 40753)	Jan. 1, 1939; United Kingdom (T. D. 49753)	Jan. 1, 1939; United Kingdom (T. D. 49753).		Jan. 1, 1939; United Kingdom (T. D. 49753).	Jan. 1, 1939; United Kingdom (T. D. 49753)	Jan. 1, 1939; United Kingdom (T. D. 49753).
10% ad val	12½% ad val	10% ad val*	7½% ad val	15% ad val	15% ad val	10% ad val		10% ad val	20% ad val	20% ad val
15% ad val	15% ad val	15% ad val	} 10% ad val	20% ad val	20% ad val	15% ad val		10% ad val	25% ad val	25% ad val
(4) Side upper leather, etc.—Continued. Side upper splits, wax or rough, not cut or wholly or partly manufactured into uppers, vamps, or any forms or shapes suitable for conversion into boots, shoes,	or tootwear. Other	(4) Patent leather, rough, partly finished, or finished,	or cut or wholly or partly maintractured into uppers, vamps, or any forms or shapes suitable for conversion into boots, shoes, or footwear.	(5) Collar, bag, case, glove, garment, or strap leather, in the rough, in the white, crust, or russet, partly	inished of initined. (6) Leather to be used in the manufacture of footballs, basket balls, soccer balls, or medicine balls.	(7) All other, rough, partly finished, finished, or curried, not specially provided for.	1530 (c) Leather (except leather provided for in subparagraph (d) of paragraph 1530 of the Tariff Act of 1930), in the rough, in the white, crust, or russet, partly finished, or finished.	If made from sheep or lamb skins: If made from sheep or lamb skins: Imported to be used in the manufacture of boots, shoes, or footwear, or cut or wholly or partly manufactured into uppers, vamps, or any forms or shapes suitable for conversion into boots, shoes,	or footwear. Other, not including chamois	If made from goat or kid skins, and not imported to be used in the manufacture of boots, shoes, or footwear, or cut or wholly or partly manufactured into uppers, vamps, or any forms or shapes suitable for conversion into boots, shoes, or footwear.
1530 (b)							1530 (c)			•

Superseded

Dutiable List—(Continued)

Articles and imported from rentile ckins or charf- ckins and imported	Rate changed	Modified rate	Effective date and basis of change
to made from repute skins of shark skins, and imported to be used in the manufacture of boots, shoes, or footwear, or cut or wholly or partly manufactured into uppers, vamps, or any forms or shapes suitable for conversion into boots, shoes, or footwear.	10% ad val	10% ad val	Jan. 1, 1935; United Kingdom (T. D. 49753).
Ingental teatures. If imported to be used in the manufacture of boots, shoes, or footwear, or cut or wholly or partly manufactured into uppers, vamps, or any forms or shapes suitable for conversion into boots, shoes, or footwear.	10% ad val	10% ad val	Jan. 1, 1939; United Kingdom (T. D. 49753).
	(25% ad val	15% ad val	Mar. 7, 1931; sec. 336
Other	15% ad val	12½% ad val	Jan. 1, 1939; United Kingdom (T. D. 49753)
Chamois leather not imported to be used in the manu- iacture of boots, shoes, or footwear, nor cut or wholly or partly manufactured into uppers, vamps, or any forms or shapes suitable for conversion into boots, shoes, or footwear.	25% ad val	20% ad val	June 15, 1936; France (T. D. 48316).
Glove and garment leather made from hides or skins of animals (including fish, reptiles, and birds, but not including sheep, lambs, goats, kids, pigs, hogs, or cettle of the bovine species), not imported to be used in the manufacture of boots, shoes, or footwear, or cut or wholly or partly manufactured into uppers, vamps, or any forms or shapes suitable for conversion into boots, shoes, or footwear,	25% ad val	15,°c ad val	Jan. 1, 1939; United Kingdom (T. D. 49733).
Rough-tanned walrus leather, not imported to be used in the manufacture of boots, shoes, or footwear, or cut or wholly or partly manufactured into uppers, vamps, or any forms or shapes suitable for conversion into boots, shoes, or footwear.	25% ad val	15% ad val	Jan. 1, 1939; United Kingdom (T. D. 49733).

	GOVE	RNM				/L.4T10		
Jan. 1, 1939; United Kingdom (T. D. 49753).	Jan. 1, 1939; United Kingdom (T. D. 49753).		Jan. 1, 1932; sec. 336	(I. D. 45511). Apr. 16, 1938; Czecho-	Apr. 16, 1938; Czecho- slovakia (T. D. 49458).	(Jan. 1, 1932; sec. 33, (T. D. 45311). Feb. 15, 1936; Switzer-	Jan. 1, 1939; United Kingdom (T. D. 49753).	Apr. 16, 1938; Czecho-slovakia (T. D. 49458).
10% ad val	20% ad val		30% ad vala	20% ad val	10% ad val ²	10% ad val	50c per pair, but not less than 10 nor more than 20% ad val.	20% ad val'
10% ad val	30% ad val		[20% ad val	30 or 20% ad val	20% ad val	20% ad val	20% ad val	20% ad val
1530 (c) Vegetable-tanned rough leather made from goat or sheep skins (including those commercially known as Indiatanned goat or sheep skins).	Leather made from hides or skins of cattle of the bovine species, grained, printed, embossed, ornamented, or decorated, in any manner or to any extent (including leather finished in gold, silver, aluminum, or like effects), or by any other process (in addition to tanning) made into fancy leather, and any of the foregoing cut or wholly or partly manufactured into uppers, vamps, or any forms or shapes suitable for conversion into boots, shoes, or footwear, all the foregoing by whatever name known, and to whatever use applied.	Boots, shoes, or other footwear (including athletic or sporting boots and shoes), made wholly or in chief value of	leather, not specially provided for:	Sewed or stitched by the process or method known as McKay.	Having molded soles laced to uppers	Turn or turned boots and shoes	Made by the process or method known as welt	Other (except moccasins)
1530 (c)	(q)	1530 (e)						
	•							

¹ The agreement contains a proviso that if total imports from all sources in any year of the classes of footwear covered by the agreement exceed it percent, in quantity, of the average annual domestic production for the preceding 5 years, of "hoots, shoes, and slippers, other than rubber," as reported by the Bureau of the Census, the United States may, after consultation with Czechoslovakia, increase the rates of duty on imports in excess of this percentage on any or all of the classes of shoes covered by the agreement.

² The proclamation did not apply to McKay sewed "other footwear."

Dutiable List—(Continued)

Effective date and basis of change	Jan. 1, 1939; Canada (T. D. 49752).		35% ad val. on Mar. 3, 1933; sec. 336 American sell- T. D. 46158).	Apr. 16, 1938; Czecho-slovakia (T. D. 49458).	Jan. 1, 1939; United Kingdom (T. D. 49753).	Jan. 1, 1939; United Kingdom (T. D. 49753).	Jan. 1, 1939; United Kingdom (T. D. 49753).
Modified rate	15% ad val		35% ad val. on American sell- ing price	25% ad val ¹	20% ad val	20% ad val	15% ad val
Rate changed	20% ad val.		35% ad val	35% ad val	35% ad val	35% ad val	15% ad val
Articles	Skating boots and shoes, made wholly or in chief value of leather, sewed or stitched by the process or method known as McKay, if attached to ice skates, and not specially provided for.	Boots, shoes, or other footwear (including athletic or sporting boots and shoes), the uppers of which are composed wholly or in chief value of wool, cotton, ramie, animal hair, fiber, rayon, or other synthetic textile, silk,	or substitutes for any of the lonegoing. With soles composed wholly or in chief value of india rubber or substitutes for rubber.	With soles composed wholly or in chief value of leather.	f) Harness valued at more than \$70 per set, single harness valued at more than \$40, saddles valued at more than \$40 each, saddlery, and parts (except metal parts) for	any of the foregoing. Saddles made wholly or in part of pigskin or imitation pigskin.	Saddles and harness, not specially provided for, and parts thereof, except metal parts, finished or unfinished.
Far. No.	1530 (e)	1530 (e)			1530 (f)	1530 (f)	1530 (f)

2 Rate reduced pursuant to trade agreement with Czechoslovakia.

		GOVERNMENT REGULATIONS									95
	Effective date and basis of change	Jan. 1, 1936; Canada (1. D. 48033). Jan. 1, 1939; Canada (T. D. 40752).	497.52). Jan. 1, 1939; Canada (T. D. 49752).	Feb. 1, 1936; Netherlands (T.	Duty-free status bound Jan. 1, 1939; United Kingdom (T. D. 49753).	Jan. 1, 1939; United Kingdom (T. D. 49753).	Jan. 1, 1939; United Kingdom (T. D. 49753).	48034), Mar, 2, 1936; Honduras (T. D. 48131), June 15, 1936; Guatemala (T. D. 48317). Oct. 1, 1936; Nicaragua (T. D. 48317). AS511), Aug. 2, 1937; Costa Rica (T. D. Aug. 2, 1937;	May 20, 1936; El Salvador (T. D. 48947). Feb. 1, 1936; Netherlands (T. D. 48075). May 20, 1936; Colombia (T. D. 48258). Oct. 1, 1936; Nicaragua (T. Oct. 1, 1936; Nicaragua (T.	L. 48311). Aug. 2, 1937; Costa Rica (T. D. 49072). May 31, 1937; El Salvador (T. D. 48947). Oct. 23, 1938; Ecuador (T. D. 46710).	Duty-free status bound Jan. 1, 1939; United Kingdom (T. D. 49753).
		puno	puno	puno	puno	punoc	punoc	punoq		punoq	ponuq
	Tariff status	tatus b	tatus b	tatus b	tatus E	tatus l	status l	status 1		status 1	status
		Duty-free status bound	Duty-free s	Duty-íree s	Duty-íree s	Duty-íree s	Duty-free	Duty-free		Duty-free status bound	Duty-free
Free List	Articles	Furs and furskins, not specially provided for, undressed: Mink, beaver, muskrat, and wolf	Prairie wolf, skunk, otter, lynx, and fisher	Moleskins	Caracul, ermine, fitch, fox (other than silver or black fox) lamb, kid, sheep, goat, marten, monkey, pony, sable, skunk, and squirrel.	Goldbeaters' molds and goldbeaters' skins	Hides and skins of the India water buffalo imported to be used in the manufacture of rawhide articles.	1765 Deerskins, raw		Reptile skins, raw	Seal skins (not fur seal skins), raw
	Far. No.	1681				1683	1691	1765		1765	1765

of duty or duty-free status are bound in trade agreements. Changes made in the paragraphs of the Tariff Act of 1930 given above are listed below, preceded by some of the explanatory notes of the Tariff Commission. They are complete to May 6, 1940; for possible changes made after that date, the reader is requested to write directly to the United States Tariff Commission. The paragraphs referred to are the same as those given above. Where no reference is made to a section of a paragraph, as for example, Paragraph 1530 (a), it means that no change has been made in this section.

For the purpose of showing the history of tariffs since 1930, certain interim changes in duty have been included, even though such changes have been superseded. Such superseded items are indicated by an asterisk (*).

The effective dates of changes and whether they were made by amendatory legislation, under section 336, or by a trade agreement proclamation, are indicated in the last column. The appearance of the name of a country after the date indicates that the duty was changed or bound against increase pursuant to a trade agreement with that country. Where more than one effective date and basis of change appears in conjunction with a particular modified rate, such rate has been continuously in effect from the first date shown.

The foreign trade agreements were proclaimed under the Trade Agreements Act of June 12, 1934, as extended by Public Resolution 10, approved March 1, 1937. This act provides that rates of duty proclaimed thereunder shall apply to products of all countries unless the President suspends their application to products of a country which discriminates against the commerce of the United States or pursues acts or policies which in his opinion tend to defeat the purposes of the Trade Agreements Act.

Section 336 herein referred to is the so-called flexible tariff rate adjustment provision of the Tariff Act of 1930. Where a duty has been changed under this section and again changed pursuant to a trade agreement, both changes are shown, inasmuch as the rates established under section 336 still apply to products of Germany.

By virtue of the President's action pursuant to the Trade Agreements Act, duties that have been changed under the trade agreements have not been applicable to products of Germany entered on and after October 15, 1935. Goods produced in the territory formerly known as Austria have been considered as of German-origin beginning May 6, 1938. Goods produced in the Sudeten areas occupied by Germany have been considered as German if exported to the United States on or after November 10, 1938.

From August 1, 1936, to February 1, 1938, the products of Australia were not entitled to trade agreement rates.

On February 8, 1938, the President by proclamation directed that the duty concessions made to Nicaragua should terminate on March 10, 1938. Because of other agreements, this action has not resulted in actual changes in United States duties.

In general, rates on Cuban products are 20 percent less than the lowest rates accorded products of other foreign countries, except where a still lower rate applicable to Cuban products is indicated herein. Some products of Cuba are free of duty, although like products are dutiable from other foreign countries. The rates of duty shown in the pamphlet in conjunction with the parenthetical phrase "from Cuba" apply exclusively to Cuban products, and not to the products of any other country.

Sanitary Control

Because of the necessity for strict compliance with the law in the importation of hides and skins, the regulations of the Bureau of Animal Industry are given below in full.

(B. A. I. Order 371)¹

Effective on February 1, 1940

Issued May 6, 1940

United States Department of Agriculture

Bureau of Animal Industry

Under authority vested in the Secretary of Agriculture by law the following regulations are issued for the purpose of preventing the introduction from foreign countries into the United States of communicable diseases of livestock. These regulations supersede all previous regulations governing the sanitary control of animal byproducts, hay and straw offered for importation and shall become effective on February 1, 1940.

Done at Washington this 27th day of October 1939.

Witness my hand and the seal of the Department of Agriculture.

HARRY L. BROWN, Acting Secretary of Agriculture.

Part 95—Sanitary Control of Animal Byproducts (Except Casings), and Hay and Straw, Offered For Entry Into the United States

[Secs. 95.1 to 95.27, inclusive, issued under the authority contained in Sec. 2, 32 Stat. 792; 21 U. S. C. 111]

REGULATION 1

Sec. 95.1. Definitions.—Whenever in these regulations the following words, names, or terms are used they shall be construed, respectively, to mean:
(a) Department—United States Department of Agriculture.

- (b) Bureau.—The Bureau of Animal Industry, United States Department of Agriculture.
 - (c) Chief of Bureau.—Chief of the Bureau of Animal Industry. (d) Inspector.—An inspector of the Bureau of Animal Industry.

(v) Consular officer.—A consular officer of the United States of America.

(f) Approved establishment.—An establishment approved by the Bureau for the receipt and handling of restricted import animal byproducts.

(g) Approved warehouse.—A warehouse having facilities approved by the Bureau for the handling and storage, apart from other merchandise, of restricted import products.

- (h) Approved chlorinating equipment.—An equipment approved by the Bureau as efficient for the disinfection of effluents against the contagions of foot-and-mouth disease and rinderpest.
- (i) Approved sewerage system.—A drainage system equipped and operated so as to carry and dispose of sewage without endangering livestock through the contamination of streams or fields and approved by the Bureau.
- (j) Animal byproducts.—Hides, skins, hair, wool, glue stock, bones, hoofs, horns, bone meal, hoof meal, horn meal, blood meal, meat meal, tankage, glands, organs, or other parts or products of ruminants and swine unsuitable for human consumption.
- (k) Glue stock.--Heshings, hide cuttings and parings, tendons, or other collagenous parts of animal carcasses.
 - (1) Bone meal.—Ground or crushed animal bones.
 - (m) Blood meal.—Dried blood of animals.
- (n) Meat meal or tankage.—The rendered and dried carcasses or parts of the carcasses of animals.
- (o) Hay and straw.—Dried grasses, clovers, legumes, and similar materials or stalks or stems of various grains, such as barley, oats, rice, rye, and wheat.

¹ Supersedes B. A. I. Order 341 and all amendments thereto. The numbering of the parts and sections of B. A. I. orders conforms to the numbering in title 9, chapter 1, of The Code of Federal Regulations.

REGULATION 2

Sec. 95.2 Country of origin.—No products or materials specified in these regulations shall be imported unless there be shown upon the consular invoice, or in some other manner satisfactory to the Chief of Bureau, the name of the country of origin of such product or material, provided that the country of origin shall be construed to mean (a) in the case of an animal byproduct, the country in which such product was taken from an animal or animals, and (b) in the case of other materials, the country in which such materials were produced.

REGULATION 3

SEC. 95.3. Byproducts from diseased animals prohibited.—The importation of any animal byproduct taken or removed from an animal affected with anthrax, foot-and-mouth disease, or rinderpest is prohibited.

REGULATION 4

SEC. 95.4. Importations from Canada.—No requirement or condition of the following regulations shall be construed to apply to products or materials specified in this order, originating in Canada and imported directly therefrom. Such products and materials not originating in but imported into the Dominion of Canada from another foreign country may be imported therefrom into the United States without compliance with the following regulations, when accompanied by a certificate signed by a veterinarian in the employ of and receiving a salary from the Canadian Government stating that they have been imported into Canada in full compliance with the Canadian regulations, provided such regulations are found by the Bureau to be the substantial equivalent of those contained in this order.

REGULATION 5

SEC. 95.5. Untained hides and skins; requirements for unrestricted entry. Untained hides and/or skins of cattle, buffalo, sheep, goats, other runninants, and swine which do not meet the conditions or requirements specified in any one of paragraphs (a) to (e) following shall not be imported except subject to handling and treatment in accordance with section 95.6 of this order after arrival at the port of entry:

(a) Hides or skins originating in and shipped directly from a country not declared by the Secretary of Agriculture to be infected with foot-and-month disease or rinderpest

may be imported without further restriction.

(b) Hides or skins may be imported without other restriction if found upon inspection by an inspector, or by certificate of the shipper or importer satisfactory to said

inspector, to be hard-dried hides or skins.

(c) Abattoir hides or skins taken from animals slaughtered under national government inspection in a country and in an abattoir in which is maintained an inspection service determined by the Secretary of Agriculture to be adequate to assure that they have been removed from animals found at time of slaughter to be free from anthrax, foot-and-mouth disease, and rinderpest, and to assure further the identity of such materials until loaded upon the transporting vessel, may be imported without other restriction if accompanied by a certificate bearing the scal of the proper department of such national government and signed by an official veterinary inspector of such country showing that the therein described hides or skins were taken from animals slaughtered in such specified abattoir and found free from anthrax, foot-and-mouth disease, and rinderpest.

(d) Hides or skins may be imported without other restriction if shown upon inspection by an inspector, or by certificate of the shipper or importer satisfactory to said inspector, to have been pickled in a solution of salt containing mineral acid and packed

in barrels, casks, or tight cases while still wet with such solution.

(e) Hides or skins may be imported without other restriction if shown upon inspection by an inspector, or by certificate of the shipper or importer satisfactory to said inspector, to have been treated with lime in such manner and for such period as to have become dehaired and to have reached the stage of preparation for immediate manufacture into products ordinarily made from rawhide.

REGULATION 6

Sec. 95.6. Untained hides and skins; importations permitted subject to restrictions.—Hides or skins offered for importation which do not meet the conditions or requirements

² Names of countries of this character will be furnished upon request. (Following the regulations

GOVERNMENT REGULATION

of section 95.5 of this order shall be handled and treated in the following manner after arrival at the port of entry:

- (a) They shall be consigned from the coast or border port of arrival to approved establishment and shall be subject to disinfection by such method are interestant the Chief of Bureau may prescribe unless the said establishment discharges drainage into an approved sewerage system or has an approved chlorinating equipment adequate for the proper disinfection of effluents; Provided, however, That upon permission of the Chief of Bureau such hides or skins may be stored for a temporary period in approved warehouses under bond, and under the supervision of an inspector: And provided further, That I. T. or in-bond shipments of hides or skins may go forward under customs seals from a coast or border port of arrival, with the approval of an inspector at said port, to another port in the United States for consumption entry subject to the other provisions of this section.
- (b) They shall be moved from the coast or border port of arrival or, in case of I. T. or in-bond shipments, from the interior port to the approved establishment in cars or trucks or in vessel compartments with no other materials contained therein, sealed with seals of the Department, which shall not be broken except by inspectors or other persons authorized by the Chief of Bureau so to do, or without sealing as aforesaid and with other freight when packed in tight cases or casks acceptable to the inspector in charge at the port of entry.
- (c) They shall be handled at the approved establishment under the direction of an inspector in a manner approved by the Chief of Bureau to guard against the dissemination of foot-and-mouth disease and rinderpest. They shall not be removed therefrom except upon special permission of the Chief of Bureau and upon compliance with all the conditions and requirements of this section relative to the movement of the said hides and skins from the port of arrival to the said establishment.

REGULATION 7

- Sec. 95.7. Wool, hair, and bristles; requirements for unrestricted entry.—Wool, hair, or bristles derived from ruminants and/or swine which do not meet the conditions or requirements specified in any one of paragraphs (a) to (e) following shall not be imported except subject to handling and treatment in accordance with section 95.8 of this order after their arrival at the port of entry: Provided, however, That no bloodstained wool, hair, or bristles shall be imported under any condition:
- (a) Such wool, hair, or bristles may be imported without other restriction if originating in and shipped directly from a country not declared by the Secretary of Agriculture to be infected with foot-and-mouth disease or rinderpest.
- (b) Wool or hair clipped from live animals or pulled wool or hair may be imported without other restriction if the said wool or hair is reasonably free from animal manure in the form of dung locks or otherwise.
- (c) Wool, hair, or bristles taken from sheep, goats, cattle, or swine, when such animals have been slaughtered under national government inspection in a country and in an abattoir in which is maintained an inspection service determined by the Secretary of Agriculture to be adequate to assure that such materials have been removed from animals found at time of slaughter to be free from anthrax, foot-and-mouth disease, and rinderpest, and to assure further the identity of such materials until loaded upon the transporting vessel, may be imported without other restriction if accompanied by a certificate bearing the seal of the proper department of said national government and signed by an official veterinary inspector of such country showing that the therein described wool, hair, or bristles were taken from animals slaughtered in such specified abattoir and found free from anthrax, foot-and-mouth disease, and rinderpest.
- (d) Wool, hair, or bristles which have been scoured, thoroughly washed, or dyed may be imported without other restriction.
- (e) Wool, hair, or bristles from a disinfecting station of a national government, methods of disinfection at which have been approved by the Secretary of Agriculture, may be imported without other restriction if accompanied by a certificate of the director or other accredited official of such station showing that said wool, hair, or bristles covered by the counsular invoice specified in said certificate have been subjected to the scouring and disinfecting process required at such station for the disinfection of wool or hair.

REGULATION 8

SEC. 95.8. Wool, hair, and bristles; importations permitted subject to restrictions.—Wool, hair, or bristles offered for importation which do not meet the conditions or requirements of section 95.7 of this order shall be handled and treated in the following manner after arrival at the port of entry:

(a) Such wool, hair, or bristles shall be consigned from the coast or border port of arrival to an approved establishment: Provided, horeever, That upon permission by the Chief of Bureau such wool, hair, or bristles may be stored for a temporary period in approved warehouses under bond and under the supervision of an inspector: And provided further, That I. T. or in-bond shipments of wool, hair, or bristles may go forward under customs seals from a coast or border port of arrival, with the approval of an inspector at said port, to another port for consumption entry, subject to the other provisions of this section.

(b) Such wool, hair, or bristles shall be moved from the coast or border port of arrival or, in the case of I. T. or in-bond shipments, from the interior port to the establishment in cars or trucks or in vessel compartments with no other materials contained therein, sealed with seals of the Department, which shall not be broken except by inspectors or other persons authorized by the Chief of Bureau so to do, or without sealing as aforesaid and with other freight when packed in tight cases acceptable to an

inspector.

(c) Such wool, hair, or bristles shall be handled at the establishment under the direction of an inspector in a manner approved by the Chief of Burcau to guard against the dissemination of foot-and-mouth disease and rinderpest. Such products shall not be removed therefrom except upon special permission of the Chief of Burcau and upon compliance with all the conditions and requirements of this section relative to the movement of the said wool, hair, or bristles from the port of arrival to the said establishment.

REGULATION 9

SEC. 95.9. Glue stock; requirements for unrestricted entry.—Glue stock which does not meet the conditions or requirements specified in any one of paragraphs (a) to (c) following shall not be imported except subject to handling and treatment in accordance with section 95.10 of this order after arrival at the port of entry:

(a) Glue stock originating in and shipped directly from a country not declared by the Secretary of Agriculture to be infected with foot-and-mouth disease or rinderpest

may be imported without other restriction.

(b) Glue stock may be imported without other restriction if found upon inspection by an inspector, or by certificate of the shipper or importer satisfactory to said inspector, to have been properly treated by acidulation or by soaking in milk of lime or a lime paste, or to have been dried so as to render each piece of the hardness of a sun dried hide.

(c) Glue stock taken from cattle, sheep, goats, or swine slaughtered under national government inspection in a country and in an abattoir in which is maintained an inspection service determined by the Secretary of Agriculture to be adequate to assure that such materials have been removed from animals found at time of slaughter to be free from authrax, foot-and-mouth disease, and rinderpest, and to assure further the identity of such materials until loaded upon the transporting vessel, may be imported without other restriction if accompanied by a certificate bearing the seal of the proper department of said national government and signed by an official veterinary inspector of such country showing that the therein described glue stock was taken from animals slaughtered in such specified abattoir and found free from anthrax, foot-and-mouth disease, and rinderpest.

REGULATION 10

SEC. 95.10. Glue stock; importations permitted subject to restrictions. Glue stock offered for importation which does not meet the conditions or requirements of section 95.9 of this order shall be handled and treated in the following manner after arrival

at the port of entry:

(a) It shall be consigned from the coast or border port of arrival to an approved establishment and shall be subject to disinfection by such method or methods as the Chief of Bureau may prescribe unless the said establishment discharges drainage into an approved sewerage system or has an approved chlorinating equipment adequate for the proper disinfection of effluents: Provided, however, That upon permission by the Chief

of Bureau glue stock may be stored for a temporary period in approved warehouses under bond and under the supervision of an inspector: And provided further, That I. T. or inbond shipments of glue stock may go forward under customs scals from a coast or border port of arrival with the approval of an inspector at said port to another port for consumption entry, subject, after arrival at the latter port, to the other provisions of this section.

(b) It shall be moved from the coast or border port of arrival or, in case of I. T. or in-bond shipments, from the interior port to the establishment in cars or trucks or in vessel compartments with no other materials contained therein, sealed with seals of the Department, which shall not be broken except by inspectors or other persons authorized by the Chief of Burcau so to do, or without sealing as aforesaid and with other freight when packed in tight cases or casks acceptable to an inspector at port of entry.

(c) It shall be handled at the establishment under the direction of an inspector in a manner approved by the Chief of Bureau to guard against the dissemination of foot-and-mouth disease and rinderpest. It shall not be removed therefrom except upon special permission of the Chief of Bureau and upon compliance with all the conditions and requirements of this section relative to the movement of the said glue stock from the

port of arrival to the said establishment.

REGULATION 11

SEC. 95.11. Bones, horns, and hoofs; requirements for unrestricted entry.—Bones, horns, and hoofs of ruminants and swine which do not meet the conditions or requirements specified in paragraph (a) or (b) following shall not be imported except subject to handling and treatment in accordance with section 95.12 of this order after arrival at the port of entry:

(a) Bones, horns, and hoofs originating in and shipped directly from a country not declared by the Secretary of Agriculture to be infected with foot-and-mouth disease

or rinderpest may be imported without other restriction.

(b) Clean, dry bones, horns, and hoofs that are free from undried pieces of hide, flesh, and sinew may be imported without other restriction.

REGULATION 12

Sec. 95.12. Bones, horns, and hoofs; importations permitted subject to restrictions.—Bones, horns, and hoofs offered for importation which do not meet the conditions or requirements of section 95.11 of this order shall be handled and treated in the following manner after arrival at the port of entry:

(a) They shall be consigned from the coast or border port of arrival to an approved establishment having facilities for their disinfection or their conversion into products customarily made from bones, horns, or hoofs: Provided, however, that I. T. or in-bond shipments of bones, horns, or hoofs may go forward under customs seals from a coast or border port of arrival, with the approval of an inspector at said port, to another port

for consumption entry subject to the other provisions of this section.

(b) They shall be moved from the coast or border port of arrival or, in case of I. T. or in-bond shipments, from the interior port to the establishment in cars or trucks with no other materials contained therein, sealed with seals of the Department, which shall not be broken except by inspectors or other persons authorized by the Chief of Bureau so to do, or without sealing as aforesaid and with other freight when packed in

tight cases or casks acceptable to an inspector at the port of entry.

(c) They shall be handled at the establishment under the direction of an inspector in a manner to guard against the dissemination of foot-and-mouth disease and rinderpest, and the bags, burlap, or other containers thereof, before leaving the establishment, shall be disinfected by heat or otherwise, as directed by the Chief of Bureau or burned at the establishment. They shall not be removed therefrom except upon special permission of the Chief of Bureau and upon compliance with all the conditions and requirements of this section relative to the movement of the said bones, horns, and hoofs.

REGULATION 13

Sec. 95.13. Bone meal, blood meal, tankage, and similar products for use as fertilizer or animal feed; requirements for unrestricted entry.—Dried blood or blood meal, lungs or other organs for use as fertilizer or as feed for domestic animals, which do not need the conditions or requirements specified in paragraph (a) or (b) following, shall not be imported. Tankage, meat meal, bone meal, born meal, boof meal, wood worsts wood

manure, and similar products for use as fertilizer or as feed for domestic animals, which do not meet the conditions or requirements specified in paragraph (u) or (b) following, shall not be imported except subject to handling and treatment in accordance with section 95.14 of this order after their arrival at the port of entry.

(a) Products specified in this section originating in and shipped directly from a country not declared by the Secretary of Agriculture to be infected with foot and-month

disease or rinderpest may be imported without further restriction.

(b) Products specified in this section may be imported without other restriction if accompanied by the certificate of a consular officer showing that in the process of manufacture the particular product was heated throughout to a temperature of not less than 156°F. (68.9°C.).

REGULATION 14

Sec. 95.14. Tankage, bone meal, and similar products for use as fertilizer or as feed for domestic animals; importations permitted subject to restrictions. Tankage, meat meal, bone meal, horn meal, hoof meal, wool waste, wool manure, and similar products which do not meet the conditions or requirements of section 95.13 of this order shall be quarantined in an approved warehouse for at least 90 days or disinfected at the port of entry, together with the bags or other containers thereof, and shall be otherwise handled as directed by the Chief of Bureau.

REGULATION 15

- SEC. 95.15. Blood meal, blood albumin, intestines, and other animal hyproducts for industrial use; requirements for unrestricted entry.—Blood meal, blood albumin, hone meal, intestines, or other animal materials intended for use in the industrial arts, which do not meet the conditions or requirements specified in paragraph (a) or (b) following, shall not be imported except subject to handling and treatment in accordance with section 95.16 of this order:
- (a) Products specified in this section originating in and shipped directly from a country not declared by the Secretary of Agriculture to be infected with foot and mouth disease or rinderpest may be imported without further restriction.
- (b) Products specified in this section may be imported without further restriction if accompanied by the certificate of a consular officer showing that in the process of manufacture the particular product was heated throughout to a temperature of not less than 156°F. (68.9°C.).

REGULATION 16

- SEC. 95.16. Blood meal, blood albumin, intestines, and other animal hyproducts for industrial use; importations permitted subject to restrictions. Blood meal, blood albumin, bone meal, intestines, or other animal materials intended for use in the industrial arts, which do not meet the conditions or requirements of section 95.15 of this order shall be handled and treated in the following manner after arrival at the port of entry:
- (a) They shall be consigned from the coast or border port of arrival to an approved establishment: Provided, however, That upon permission by the Chief of Bureau they may be stored for a temporary period in approved warehouses under bond and under the supervision of an inspector: And provided further. That I, T, or in bond shipments of such products may go forward under customs seals from a coast or border port of arrival, with the approval of an inspector at said port, to another port for consumption entry, subject after arrival at the latter port to the other provisions of this section.
- (b) They shall be moved from the coast or border port of arrival or, in the case of L. T. or in-bond shipments, from the interior port to the establishment in cars or trucks or in vessel compartments with no other materials contained therein, scaled with seals of the Department, which shall not be broken except by Eurcan inspectors or other persons authorized by the Chief of Eurcan so to do, or without scaling as aforesaid and with other freight when packed in tight cases or casks acceptable to an inspector at the port of entry.
- (c) They shall be handled at the establishment under the direction of an inspector in a manner to guard against the dissemination of foot-and month disease and rinderpest. They shall not be removed therefrom except upon special permission of the Chief of Bureau and upon compliance with all the conditions and requirements of this section relative to the movement of the said products from the port of arrival to the said establishment.

REGULATION 17

- SEC. 95.17. Glands, organs, ox gall, and like materials; requirements for unrestricted entry.—Glands, organs, ox gall or bile, bone marrow, and various like materials derived from domestic runninants or swine, intended for use in the manufacture of pharmacentical products, which do not meet conditions or requirements specified in paragraph (a) or (b) following, shall not be imported except subject to handling and treatment in accordance with section 95.18 of this order:
- (a) Such glands, organs, or materials may be imported without other restriction if originating in and shipped directly from a country not declared by the Secretary of Agriculture to be infected with foot-and-mouth disease or rinderpest.
- (b) Such glands, organs, or materials may be imported without other restriction if accompanied by the certificate of a consular officer showing that in process of preparation the particular product was subjected to a temperature of not less than 156°F. (68.9°C.).

REGULATION 18

Sec. 95.18. Glands, organs, ox gall, and like materials; importations permitted subject to restrictions.—Glands, organs, ox gall or bile, bone marrow, and various like materials derived from domestic ruminants or swine, which do not meet the requirements of section 95.17 of this order may be imported for pharmaceutical purposes if in tight containers and consigned to an approved establishment: Provided, however. That upon special permission of the Chief of Bureau they may be stored for a temporary period in approved warehouses under bond and under the supervision of an inspector. They shall be handled and processed at the said establishment in a manner approved by the Chief of Bureau and the containers shall be destroyed or disinfected as prescribed by him. They shall not be removed therefrom except upon special permission of the Chief of Bureau and upon compliance with all the conditions and requirements of this section relative to the movement of the said glands, organs, ox gall, and like materials from the port of arrival to the said establishment.

REGULATION 19

Sec. 95.19. Animal stomachs.—Stomachs or portions of the stomachs of ruminants or swine, other than those imported for food purposes under the meat-inspection regulations of the Department, shall not be imported without permission from the Chief of Bureau. Importations permitted shall be subject to such restrictions as the Chief of Bureau may deem necessary in each instance.

REGULATION 20

SEC. 95.20. Animal manure.- -Manure of horses, cattle, sheep, other ruminants, and swine shall not be imported except upon permission from the Chief of Bureau. Importations permitted shall be subject to such restrictions as he may deem necessary in each instance: Provided, however, That manure produced by animals while in transit to the United States shall be subject only to the requirements of the Department regulations governing the importation of donestic livestock and other animals.

REGULATION 21

- Sec. 95.21. Hay and straw; requirements for unrestricted entry.—Hay or straw which does not meet the conditions or requirements of paragraph (a), (b), or (c) following shall not be imported except subject to handling and treatment in accordance with section 95.22 of this order after arrival at the port of entry.
- (a) Hay or straw may be imported without other restriction if originating in and shipped directly from a country not declared by the Secretary of Agriculture to be infected with foot-and-mouth disease or rinderpest.
- (b) Hay or straw packing materials may be imported without other restriction if accompanied by a certificate of a consular officer showing that the said material had been disinfected by placing it loosely in a tight compartment and subjecting it to the action of live steam, in all parts of which compartment a temperature of not less than 176°F. (80°C.) was maintained for at least 10 minutes, or by placing it loosely in a tight compartment having a temperature of not less than 65°F. (19°C.) and spraying over and into the hay or straw 10 fluid ounces of formaldehyde solution (containing not less than 37 per cent formaldehyde by weight) for each 1,000 cubic feet of space in said compart-

ment, which was immediately closed in a manner to prevent the escape of the formalde-

hyde vapor and kept closed for not less than 8 hours.

(c) Hay or straw packing materials may be imported without other restriction if a certificate of the shipper appears on the consular invoice showing that such packing material was obtained from a disinfecting station, the methods of disinfection at which have been approved by the United States Department of Agriculture, and giving the names of the said disinfecting station and the factory or establishment where the merchandise covered by the invoice was packed: Provided, however, That in the case of goods unaccompanied by a consular invoice a like certificate appearing on the commercial invoice will be acceptable.

REGULATION 22

Sec. 95.22. Hay and straw; importations permitted subject to restrictions. Hay or straw which does not meet the conditions or requirements of section 95.21 of this order shall be handled and treated in the following manner upon arrival at the port of entry:

(a) Hay or straw packing materials shall be burned or disinfected at the expense of the importer or consignee in the manner and at the time directed by the Chief of

Bureau.

(b) Hay or straw for use as feeding material, hedding, or similar purposes shall be stored and held in quarantine for a period of not less than 90 days in an approved warehouse at the port of entry and shall be otherwise handled as directed by the Chief of Bureau.

REGULATION 23

Sec. 95.23. Previously used meat covers; conditions prohibiting importation. The importation of any cloth or burlap which has been used to cover fresh or frozen meats originating in any country declared by the Secretary of Agriculture to be infected with foot-and-mouth disease or rinderpest is prohibited.

REGULATION 24

Sec. 95.24. Methods for disinfection of hides, skins, and other materials. Hides, skins, and other materials required by these regulations to be disinfected shall be subjected to disinfection by methods found satisfactory and approved from time to time by the Chief of Bureau.

REGULATION 25

Sec. 95.25. Transportation of restricted import products; placarding cars and mark ing billing; unloading on route. Transportation companies or other operators or cars, trucks, or other vehicles carrying import products or materials moving under restriction, other than those in tight cases or casks, shall affix to and maintain on both sides of all such vehicles durable placards not less than 5½ by 6 inches in size, on which shall be printed with permanent black ink and in boldface letters not less than 13 inches in height the words "Restricted import product." These placards shall also bear the words "Clean and disinfect this car or truck." Each of the waybills, conductors' manifests, memoranda, and bills of lading pertaining to such shipments shall have the words "Restricted import product, clean and disinfect car or truck," plainly written or stamped upon its face. It for any reason the placards required by this regulation have not been affixed to each car. or the billing has not been marked by the initial or the connecting carrier, or the placards have been removed, destroyed, or rendered illegible, the placards shall be immediately affixed or replaced and the billing marked by the initial or connecting carrier, the intention being that the billing accompanying the shipment shall be marked and each car, truck or other vehicle placarded as herein specified from the time such shipment leaves the port of entry until it is unloaded at final destination and the cars, trucks, or other vehicles are cleaned and disinfected as required by section 95.26 of this order.

If it is necessary to unload en route any of the materials or products transported in a placarded car, truck or other vehicle as hereinbefore provided in this ention, the car, truck, or other vehicle from which the transfer is made and any part of the premises in or upon which the product or material may have been placed in the course of unloading or reloading shall be cleaned and disinfected by the carrier, in accordance with the provisions of section 95.26 of this order, and the said carrier shall immediately report the matter, by telegraph, to the Chief of the Bureau of Animal Industry, Washington, D. C. Such report shall include the following information: Nature of emergency; place where product or material was unloaded; original points of shipment and destination; number and initials of the original car or truck; and number and initials of the car,

truck, or other vehicle into which the product or material is reloaded in case the original car or truck is not used.

REGULATION 26

Sec. 95.26. Cars, other vehicles, boats, yards, and premises; cleaning and disinfection. —Cars, other vehicles, boats, yards, and premises which have been used in the transportation, handling, or storing of restricted import products or materials, other than those contained in tight cases or casks, shall be cleaned and disinfected under the supervision of the Bureau at the time and in the manner hereinafter provided. Except as provided in paragraph (a) following, such cars, other vehicles, and boats shall not be moved in interstate or foreign commerce until they have been so treated.

(a) Cars to be cleaned and disinfected by final carrier at destination.—Cars required by this order to be cleaned and disinfected shall be so treated by the final carrier at destination as soon as possible after unloading and before the same are moved from such final destination for any purpose: Provided, however, That when the products or materials are destined to points at which an inspector or other duly authorized representative of the Bureau is not maintained or where proper facilities cannot be provided, the transportation company shall seal, bill, and forward the cars in which the products or materials were transported to a point to be agreed upon between the transportation company and the Bureau, and the transportation company shall there clean and disinfect the said cars under the supervision of the Bureau.

(b) Methods of cleaning and disinfection.—(1) Cars, trucks, and other vehicles required by this order to be cleaned and disinfected shall be treated in the following manner: Collect all litter and other refuse therefrom and destroy by burning or other approved method, clean the exterior and interior of the cars or trucks, and saturate the

entire interior surface with a permitted disinfectant.

(2) Boats required by this order to be cleaned and disinfected shall be treated in the following manner: Collect all litter and other refuse from the decks, compartments, and all other parts of the boat used for the transportation of the products or materials covered by this order, and from the portable chutes or other appliances or fixtures used in loading and unloading same, and destroy the litter and other refuse by burning or by other approved methods, and saturate the entire surface of the said decks, compartments, and other parts of the boat with a permitted disinfectant.

(3) Buildings, sheds, and premises required by this order to be disinfected shall be treated in the following manner: Collect all litter and other refuse therefrom and destroy the same by burning or other approved methods, and saturate the entire surface of the

fencing, chutes, floors, walls, and other parts with a permitted disinfectant.

(c) Permitted disinfectant.—The disinfectant permitted for use in disinfecting cars, other vehicles, boats, yards, and premises against infection of foot-and-mouth disease and rinderpest is a freshly prepared solution containing not less than 1 pound avoirdupois of sodium hydroxide of not less than 95 percent purity to each 6 gallons of water. Commercial grades of sodium hydroxide (caustic soda) of less than 95 percent purity or commercial concentrated solutions of caustic soda may be employed, provided that in either case a sufficient quantity be used to insure that the content of the solution in actual sodium hydroxide shall be not less than I pound avoirdupois in each 6 gallons of solution.5

REGULATION 27

Sec. 95.27. Regulations applicable to products from territorial possessions.—These regulations shall be applicable to all the products and materials specified in this order which are offered for entry into the United States from any place under the jurisdiction of the United States to which the animal-quarantine laws of this country do not apply.

APPENDIX

LAW UNDER WHICH THE FOREGOING REGULATIONS ARE MADE

Extract from an Act of Congress to enable the Secretary of Agriculture to more effectually suppress and prevent the spread of contagious and infectious diseases of livestock, and for other purposes. (Approved February 2, 1903).

Sec. 2. That the Secretary of Agriculture shall have authority to make such regulations and take such measures as he may deem proper to prevent the introduction or

⁵ Caution .- Great care is necessary in handling sodium hydroxide, as it rapidly destroys organic tissues.

dissemination of the contagion of any contagious, infectious, or communicable disease of animals from a foreign country into the United States or from one State or Territory of the United States or the District of Columbia to another, and to seize, quarantine, and dispose of any hay, straw, forage, or similar material, or any meats, hides, or other animal products coming from an infected foreign country to the United States, or from one State or Territory or the District of Columbia in transit to another State or Territory or the District of Columbia whenever in his judgment such action is advisable in order to guard against the introduction or spread of such contagion. (32 Stat. 792; 21 U. S. C. 111.)

Restricted Countries

Below is given a list of the countries in which the contagious and communicable diseases of rinderpest or of foot-and-mouth disease have been found to exist as of May 6, 1940. All hides and skins from these countries must be handled in accordance with the regulations of the Bureau of Animal Industry. Unrestricted entry is permitted from all other countries. Because the list is subject to change according to the possible finding of disease in other countries or to its eradication from any of the countries listed below, the reader is requested to keep the list up to-date by making inquiries of the Bureau of Animal Industry as occasions may arise.

Finland Palestine Africa (all countries on continent) France Paraguay Albania Germany Great Britain Philippine Islands Arabia Poland Argentina Greece Belgium Portugal Hungary Bolivia Rumania India Siam Brazil Indochina Bulgaria Spain Iran (Persia) Cevlon Straits Settlements Iraq Chile Sweden Islands of the Malay China Switzerland Archipelago Chosen (Korea) Svria Islands of the Mediter-Czechoslovakia Turkey rancan Danzig (Free City) Union of Soviet Socialist Italy Denmark Republics (Russia) Luxembourg Ecuador Uruguay Federated Malay States Netherlands Yugoslavia

Methods of Disinfection of Restricted-import Hides and Skins

The Bureau of Animal Industry permits restricted hides and skins to be disinfected in the first soak water of the tannery operations by one of the following methods:

> (a) Immersion for not less than 24 hours in a 1 to 10,000 solution of sodium bifluoride (not sodium fluoride.)
> (b) Immersion for not less than 24 hours in a 1 to 7,500 solution of sodium

silicofluoride.

"By either method a fresh solution is to be used for each vat of hides or skins and not more than one part of hide or skin to each 4 parts of the solution, by weight, is to be placed in soak. The quantity of chemical substance required for charging the vat is to be first completely dissolved in a smaller container with the aid of heat and stirring, and this solution is to be at once run, with stirring, into the additional necessary quantity of cold water already in the vat. Particular attention is necessary in the use of sodium silicofluoride, which is soluble only slowly and to small degree.

"In lieu of disinfection by one of the processes listed above, the effluent from soak vats, mill drums, breaking machines or other equipment may be treated by one of the following methods:

(a) Heating to boiling point.

(b) Treatment with chlorine in such manner and in such amount as to secure efficient disinfection.

"For the chlorination of effluents, it is essential that a vat be provided, preferably of concrete, in which all effluents resulting from the soaking and treatment of hides or skins up to the liming process are collected. To these combined effluents, chlorine is added in the proportion of not less than 250 parts per million. Some provision must be made for agitating the contents in order to thoroughly mix the chlorine with the effluent. The chlorinated effluent must be held for a period of not less than two hours before discharge from the plant. Plans for new installations should be submitted for advance approval by the Bureau."

The various sources of sodium bifluoride and sodium silicofluoride are to be found in the Chemical Engineering Catalog.* Fluorex-T contains a mixture of 10 percent sodium bifluoride and 40 percent sodium silicofluoride and 1 lb. to each 500 gals, water is used for the disinfection of hides and skins.

* The Buyers' Guide to the Process Industries. Issued annually by Reinhold Publishing Corp., New York.

References

- United States Department of Agriculture, Bureau of Animal Industry Orders 370 and 371, 1939, U. S. Government Printing Office, Washington.
 United States Government, Tariff Act of 1930. U. S. Government Printing Office, Washington.
- (283 pages, price 20c).
 United States Tariff Commission. Changes in import duties since the passage of the Tariff Act of 1930, 1939. U. S. Government Printing Office, Washington. (171 pages, price 45c).

Chapter 5

Hide Damages

Hides and skins are not only perishable commodities, but they are often seriously damaged while still on the living animals. The branding of cattle for purposes of identification is widely practiced, and cattle kept in barbed-wire enclosures frequently become so badly scratched as greatly to lower the value of their hides for making fine leathers. They frequently become infested with parasites which cause serious damages to their hides, and many forms of disease prevalent among cattle also injure their hides.

After the slaughter of an animal, its hide may be badly damaged by poor flaying. Being readily putrescible, hides suffer great damage when the curing is delayed or is done carelessly and ineffectually. Accidents and carelessness during shipment of hides and skins to the tannery add to the great variety and number of damages of the raw stock as received at the tannery.

A knowledge of the various types of damage common in hides and skins is important to the tanner both in making proper selections of raw stock and in handling it to best advantage. The Tanners' Council of America has sponsored many investigations of hide damage in the hope of lessening the enormous economic losses in leather values by a campaign of education. We are indebted to Dr. Fred O'Flaherty, Director of the Council's Department of Leather Research, and to Mr. Joseph Shine, Director of the Tanners' Hide Bureau, for much of the information and many of the photographs presented in this chapter. Many of their papers on this subject appeared in the weekly magazine "Hide & Leather & Shoes" and we are indebted to Hide and Leather Publishing Co. for the use of the cuts.

Damages Occurring on Living Animals

In the hope of reducing the damages occurring on living animals, the Tanners' Council is carrying its campaign of education to the cattle raisers, showing them how greatly to reduce damages from branding, scratching, etc. and helping them to eradicate parasites and diseases among cattle.

Mechanical Damages

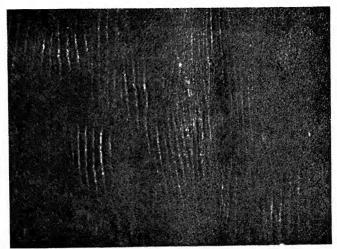
Scratches

One of the commonest types of damage found on cattle hides and skins is scratches caused by barbed-wire fences, nails, thorns and other sharp objects in fields and corrals. Cattle and other live-stock often feel the urge to scratch themselves, and barbed wires furnish them with relief from this urge. Often the hides or skins are cut to a considerable depth, subjecting the animal to infection by disease germs and inviting flies to lay their eggs in the wounds. These types of infection not only cause the production of an inferior quality of meat, but may also cause the carcass to be condemned as unfit for human consumption. Economic losses from scratches are estimated at many millions of dollars annually. Even where no infection occurs, the value of the hides for making leather is greatly

lowered. The scratches not only give the leather an unsightly appearance, but cause a considerable loss in strength where the scratches are deep and subject the leather to dangerous failures.

Immediately after the scratching, as will be recalled from Chapter 1, fibroblasts from the blood streams migrate to the region of damage and try to repair it by producing scar tissue, which does not behave like the normal collagen fibers in the various tannery operations. For some types of leathers, the scratched areas cannot be used at all.

Because of the hair, a tanner cannot see the scratches when he buys a hide or skin. He may pay for a healthy whole skin and then find it almost worthless after he has unhaired it. His only source of protection against scratch damages is to keep careful records of the sources of his raw stock and then avoid those where scratch damages seem excessive. Meanwhile the campaign goes on to educate cattle raisers, in their own interest as well as that of others, to replace barbed-wire fences by smooth-wire fences and to remove nails, thorn hedges, etc. from the fields and pens where animals are confined.



Courtesy Hide and Leather Publishing Co.

Fig. 55. Unsightly Healed Sears on Upper Leather Caused by Curry-Comb Scratches.

Although most of the scratch damages are caused by barbed wires, a considerable amount of damage is done by the use of curry combs, particularly on calves, in the removal of dry filth crusts. Fig. 55 shows the grain surface of a piece of shoe-upper leather rendered valueless by curry-comb scratches. An attempt is being made to educate farmers not to use curry combs with sharp teeth and to soak and soften filth before attempting to remove it from an animal.

Another serious type of damage is caused by goads, prod poles, pitchforks and other pointed instruments, which cause scratches and actual punctures, usually in the most valuable parts of the hides.

Wire Damages

Many ignorant and superstitious cattle raisers still observe the ancient and inhuman practice of placing wires in the hides of their cattle, a relic of witchcraft



? Courtesy Hide and Leather Publishing Co.
Fig. 56. Dangerous Wires Placed in Hides, a Relie of Witchcraft Days.

days. Heavy copper or iron wires are forced through the loose folds of the dewlap, brisket or flanks and then twisted to keep them in place.

Outbreaks of serious cattle diseases have been traced to such practice. Not only are the hides injured, but the wires cause serious damage to knives and



Courtesy Hide and Leather Publishing Co. Fig. 57. Brand Marks on Sole Leather.

machinery in both slaughter house and tannery. Fig. 56 shows some of these wires found in cattle hides as received at the tannery. Metal identification tags placed in hides belong in the same category.

Brands

It is a widespread practice to brand animals with hot branding irons for identification purposes, and often the branding is done on the most valuable portions of the hides. Branding causes severe and painful burns, which gradually heal by the formation of scar tissue. The unsightly appearance of the leather caused by



Fig. 58. Cross-section of Steer Hide with Grub Working Its Way from the Flesh Side to Outer Surface.

branding results in a loss of nearly 40 percent in the value of a hide. Fig. 57 shows the effect of hot-iron branding on the appearance of the leather. A movement is on foot to replace hot-iron branding by a marking with chemicals placed only on the check for identification purposes.

Damages by Parasites and Diseases

Grubs

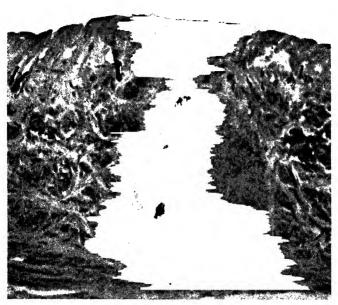
The grub or warble fly has often been referred to as "livestock public enemy No. 1." O'Flaherty and McLaughlin have made some interesting histological studies of the effects of grubs upon animal skin, from which we quote freely.

There are two species of the grub fly, the Hypoderma lineatum and the Hypo-



Courtesy Hide and Leather Publishing Co.

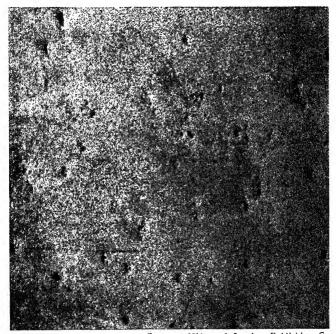
Fig. 59. Cross-section of Steer Hide from Which Grub Has Just Escaped.



Courtesy Hide and Leather Publishing Co.

in. 60. Cross-section of Steer Hide after Grub Damage Has Been Healed by the Formation of Scar Tissue.

derma bovis; the former deposits several eggs in a row, while the latter lays them singly. "The eggs are laid on the animal's hair, generally near its heel; a single fly being capable of depositing during its life from 200 to 500 eggs. In less than a week the eggs are hatched and liberate larvae. The liberated larvae now travel down the hair and enter the animal's skin through the hair follicle openings or the associated glands. Within a day or two after the entrance of the larvae a small scab forms to close the opening they have left. Once under the skin's surface the larvae penetrate the skin corium and reach the underlying connective tissue of the flesh. From this period until the grub appears in the region of the animal's backbone but little is known definitely. While in the animal body the larvae



Courtesy Hide and Leather Publishing Co.

Fig. 61. Healed Grub Damages on Heavy Leather.

undergo a number of molts, during which time they travel, by an undetermined route, through the entire body, appearing to select loose connective tissue for their path.

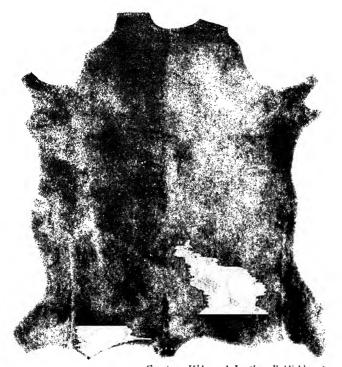
"After two previous molts the larvae have developed into the third stage and have reached the flesh immediately underlying the animal's skin, usually near its back-bone. Since they have to spend considerable time at this spot they proceed to provide quarters in keeping with their needs. They first burrow out a considerable space in the hide's "flesh"; the bulk of the grub's body remains in this flesh space until its escape from the animal through the skin. They next arrange breathing communication with the outside atmosphere by burrowing through the corium and epidermis; the opening thus formed is known as the breathing pore.

"While living in the space described above the larvae undergo two further

molts, developing into their fifth and final stage and ultimately escape through the breathing pores. Should the animal be slaughtered before their escape (or very soon afterward) the hide would show "open grubs." If escape has preceded slaughter sufficiently long (so that nature has had time to heal the wound by the formation of "scar tissue"), the hide will show "healed grubs." It is evident that the severity of healed grub damage to skin varies with the length of time elapsing between the grub's escape and the slaughter of the animal.

"The grub digests and destroys the skin around it, and deposits, in the cavity described above, waste products of its own metabolism. This waste debris, or part of it, often remains in the skin after the grub's escape, being walled off and more or less permanently enclosed by the scar tissue formed. The points at which skin has been weakened by the digestive action of grubs may become infected by bac-

teria, and in such cases abscesses may result."



Courtesy Hide and Leather Publishing Co.
Fig. 62. Calf Leather "Riddled" with Grub Holes.

Fig. 58 shows a photomicrograph of a cross-section of steer hide cut right through a grub working its way upward from the flesh side toward the outer surface and destroying the hide fibers in its path. Fig. 59 shows a cross-section of steer hide cut through the hole left after the grub has departed.

If the animal is still alive after the grub has gone, fibroblasts from the blood try to repair the damage by producing scar tissue. Fig. 60 shows a cross section of steer hide after the healing action has taken place and the hole is completely filled with scar tissue.

Even when the grub has left and the damage has been repaired with scar tissue, leather made from the hide is unsatisfactory, both from the standpoint of appearance and of strength.

Fig. 61 shows the surface of heavy leather with many healed grub damages. Fig. 62 shows a skin of calf leather with grub holes, or "pepper boxes," which look like holes made by buckshot.

The Department of Agriculture has made exhaustive studies of the grub fly, which does but little travelling during its lifetime, and has come to the conclusion that any farm or community can reduce or entirely eliminate grubs in from one to two years by following the plan it has laid down in "Farm Bulletin No. 1596."

Lice

Animal lice are small parasitic organisms that live on animals and are generally differentiated according to species as sucking lice or biting lice. In laying their eggs, they attach them to the hairs of the animal close to the skin. It requires about two weeks for the eggs to hatch and a shorter period for maturing, at which time the females are ready to mate and begin an egg-laying period. The lice spend their entire lives on the animal host.

Not only is the grain surface of the leather scarred by the lesions made by lice, but a loose and readily decomposing spot is produced by the inflammation at the site where the lice attach themselves.

Lice are readily destroyed and the Department of Agriculture has issued a bulletin on "Cattle Lice and How to Eradicate Them." This can be obtained as "Farm Bulletin No. 909."

Ticks

The tick is another blood-sucking parasite that lives on animals. Their development is described by O'Flaherty and Roddy as follows:

"Ticks are parasites which live on various species of animals—they not only devitalize and annoy the animals attacked, but often are carriers of serious systemic diseases.

"The tick, of which there is one or more species for each species of animal, is a small bug-like animal. Its body is large; it has a small head and chest and four pairs of

legs. The head has mandibles (jaws) and a hypostome—a sort of a radio-dart.

"There are male and female ticks which live on the animal skin, and the female attaches itself by its mouth parts and sucks blood. While so attached, mating occurs and after about three weeks of blood sucking the female falls to the ground and finds a secluded spot where she lays her eggs. A single female will lay as many as 4,000 to 5,000 eggs. The preferable place for egg laying is under a stone.

"In about three weeks of proper temperature the eggs hatch and the larvae, which are small and have only three pair of legs, crawl about on grass or other plant life, from where they come in contact with the animals they parasitise. These larvae are

able to live in a bottle for 6 months without food.

"As soon as the tick larvae finds a home on the skin of some animal it undergoes a number of developmental changes and matures into male and female 8 legged ticks. The process then commences anew.

The favorite spots where ticks prefer to attach themselves is such protected places as on the tender skin between the fore legs of the cattle. When quite numerous the

ticks attach themselves at any point on the skin.

"Because the female attaches itself by inserting a claw covered head, a certain amount of local damage is done at the site of attachment. Because blood is sucked out of the fine capillaries, tissue damage results. The part becomes congested and inflamed.

"As the tick is the carrier for such diseases as Texas Fever or Splenic Fever, it often happens that some of the germ life which causes these diseases are instilled

when such attack is made.

"The damage done by ticks is, therefore, threefold: ticks damage the skin; ticks

suck blood and weaken the animals attacked; ticks carry contagious disease germs and inject them into animals.

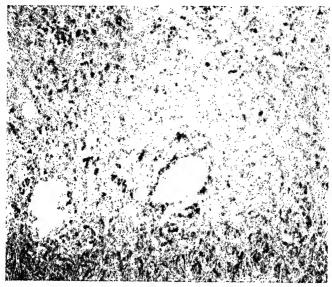
"Full details of the seriousness of Cattle Fever ticks are set forth in the U. S. Dept.

of Agriculture Bulletin No. 1057. All live stock raisers should read this booklet.

"When tick damaged skins are made into leather, the grain shows the damage where the ticks were attached which lower the value and beauty of such leather. The spots under such scars are loose and often badly decayed."

Fleas

Fleas are a common type of insect frequently found living on the skins of animals. They have compressed bodies, limbs adapted for leaping and heads armed with piercing mandibles, or jaws. They are also equipped with long extensions of the nose for sucking blood. They cause skin damages, which are small at first, but may be the forerunners of serious secondary infections. They also play the role of host to some species of intestinal worms.



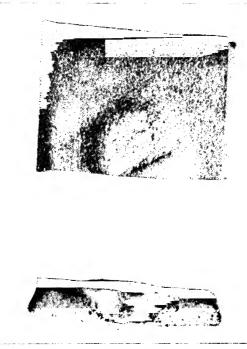
Courtesy Hide and Leather Publishing Co.

Fig. 63. Cross-section of Hide with Voids Between the Fibers Caused by Mange Mites.

Mange

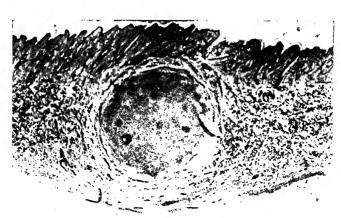
Mange is a broad name given to many different parasitic skin diseases of animals, one of the commonest types being known as follicular, or demodectic mange. This disease is described by O'Flaherty and Roddy as follows:

"Follicular mange is a contagious parasitic disease which affects all species of animals, including man. This form of mange is caused by a mite which is visible only under the microscope. It lives in the hair follicles and beneath the skin's surface. This form of skin disease is difficult to detect and identify, a fact which accounts for its spread among cattle and swine herds. Mange damage to the animal's skin becomes apparent in the early stages of preparing the skins or hides for tanning. The damage done by follicular mange greatly reduces the value of the leather made from such skins or hides. The mange mites, male and female, enter the skin through the follicles where they mate. The females then move to a space between the fibers below the



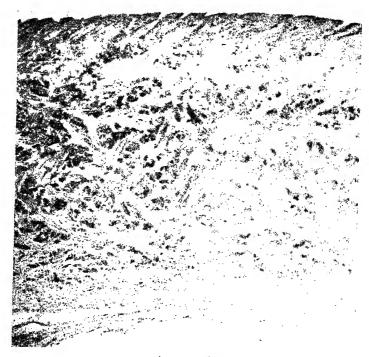
Courtesy Hide and Leather Publishing Co.

Fig. 64. Lesions of Follicular Mange in a Piece of Calf Skin. (In the finished leather, the mites make cheesy spots.)



Courtesy Hide and Leather Publishing Co.

Fig. 65. Cross-section of Steer Hide with Aggravated Lesion of Follicular Mange Involving more than Half the Thickness of the Hide.



Courtesy Hide and Leather Publishing Co.

Fig. 66. Cross-section of Steer Hide with Damage Caused by Follicular Mange

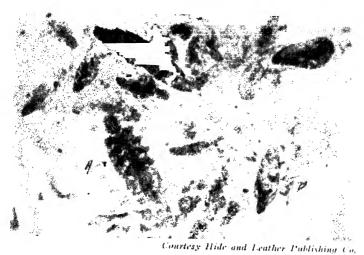


Fig. 67. Microscopic Mites Causing Follicular Mange.

level of the hair roots and lay hundreds of eggs from which young mange mites are born. The young mites undergo several changes and then when mature spread to other locations to continue their multiplication.



Courtesy Hide and Leather Publishing Co.
Fig. 68. Crust Formed by Bacteria on Mange-Infected Steer Hide.

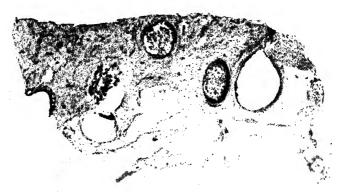
"When cattle have follicular mange, they evidence irritation of the skin if examined closely, otherwise it may not be detected for a long period of time. Animals with this or any other form of mange will scratch and rub their skins on any object available. This adds to the damage and reduces further the value of the skins or hides.

"When animals are infested with follicular mange they are unthrifty and thus

unprofitable to the owner.

"Very often the first readily noticeable indications of mange on the skins of animals are bacterial infected lesions. Very early the hair becomes dull and matted by serious discharge. By rubbing and scratching the cattle infect the "mangy" irritated areas and pus formation and skin abscesses result. These the live stock owner can easily see.

"Follicular mange is spread by contact from animal to animal or from premises to animal. Healthy animals become infected by mangy animals or from infected quarters.



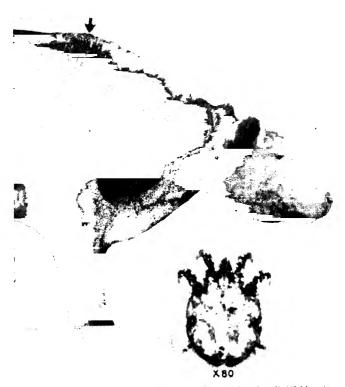
Courtesy Hide and Leather Publishing Co.

Fig. 69. Cross-section of Hog Skin with Lesions Caused by Follicular Mange.

"Since the mites for the most part are located in the depth of the skin or hide, any treatment applied locally will be only slightly effective. Animals with mange should be kept by themselves and marketed as quickly as possible. All premises on which infected animals were kept should be thoroughly cleaned and disinfected before being used by other animals.

"When skins or hides with mange are processed into leather, a great loss is suffered. The grain is coarse and scarred and with prominent hair pockets. In the substance of the leather the mites exist as cheesy masses, some such masses occupy as much as one-half the thickness of the hide.

"A great loss is suffered by the live stock owner, the packer, and the tanner when mange is present. The remedy rests with the owner of the live stock and he will profit directly with his efforts to combat the disease.



Courtesy Hide and Leather Publishing Co.

Fig. 70. The Point at Which Scabies Usually Begins on the Shoulder of Cattle and Spreads to All Parts of the Hide and (insert) the Parasitic Mite Causing Scabies.

Scabies

Another variety of mange is known as scabies, a contagious skin disease of animals caused by a parasitic mite. It is described by O'Flaherty and Roddy as follows:

"When cattle have scabies it so affects their skins that they are materially lowered in leather making value.

"Scabies is a source of great loss to the live stock raiser as well as the farmer,

and directly affects the packer and the tanner.

"Scabies is caused by a parasitic mite which is so small that it is difficult to see unless one uses a magnifying lens. This disease spreads by contact either directly or indirectly. It develops in a short time as there are male and female mites, and it has been estimated that the female will lay a million and a half eggs in about three months time.

"The lesions first appear on the shoulders and neck and then the mites spread to

all parts of the skin. The skin becomes red, irritated, and swollen, and later it thickens and becomes rough.

"Cattle and calves with scabies never do well-they become weak and anemic

which predisposes them to many other diseases.

"There are several varieties of this type of mange, but for the purpose of this article they will be considered collectively since the damage they do is of the same nature in all cases.

"Scabies is communicable to other animal species and also to man. The remedy in cattle is dipping in line-sulphur solution and proper hygiene. The mites are killed in short order by sunlight, but in the absence of sunlight they live 8 to 10 days when

away from the animal.

"For a comprehensive treatise on the treatment of scabies see Farmers Bulletin No. 1017 of the U. S. Department of Agriculture.

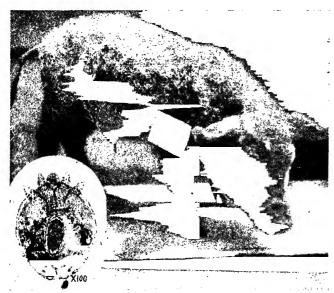
"When animals have scabies they itch and rub themselves on any object available. Any sharp objects like barb wire, nails or rough boards add to the injury of the skin and increase the damage. The skin becomes infected with bacteria and other fungi making it more difficult to cure.

"When skins of animals with scabies are made into leather the full extent of the damage is seen. The grain is rough, broken and does not uniformly take the finish. "The meat of an animal with scabies is poor and undesirable so a direct profit will be made by the farmer or stock raiser who keeps mange out of his cattle herd. "The remedy for this unnecessary economic loss which totals millions of dollars annually rests with the owners of the live stock. Eliminate mange and keep the stock in clean quarters. This will bring big dividends as profits in sales. This is the only way the damage can be eliminated from leather.

"Mange is a robber of profits to the live stock meat and leather industries. It

"Mange is a robber of profits to the live stock, meat and leather industries. It has been reduced by the cooperation of Federal and State Agricultural Departments

and the farmer, but the losses still amount to millions of dollars each year.



Courtesy Hide and Leather Publishing Co.

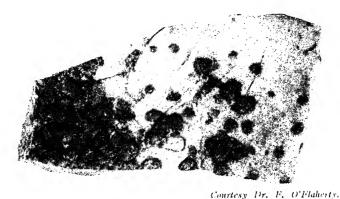
Fig. 71. Mangy Hog and (insert) the Parasitic Mite Causing Scabies.

Stephanofilariasis

During 1933, a new disease was discovered among cattle in Wyoming, Colorado, South Dakota and Nebraska by the Bureau of Animal Inspectors in cooperation with the Zoological Division and reported by Dikmans. It is caused by a small nematode worm, hair-like in size and of the genus *stephanofilaria*. It produces lesions that reduce the leather-making value of hides, which are described in detail in a paper by Roddy and O'Flaherty, to which the reader desiring more detailed information of this disease is referred.

Pox

Cow pox in cattle and hog pox in swine are infectious diseases analogous to smallpox in man. Although the diseases are no longer prevalent, it is desirable that the tanner be able to recognize damages caused by pox in order to differentiate them from other damages.



Charles, V. P. O'L'amir's

Fig. 72. Lesions on the Surface of Hog Skin Caused by Hog Pox.

In the living animal, the first symptom affecting the skin is a general inflammation and small red spots appear on the more tender parts, such as the inner thigh, abdomen and sides. The red spots develop into small vesicles or blister-like eruptions, which at first contain a thin watery serum or lymph, which become thick and pus-like. According to O'Flaherty and Roddy,



Courtesy Dr. F. O'Flaherty.

Fig. 73. Cross-section of Hog Skin Cut Through a Lesion of Hog Pox Before the Scab Had Dropped Off.

"Each lesion begins as a small pin-point sized affair, but by growth it may reach the size of a dime. In some cases several original lesions may develop into one large mass. Due to the itching nature of the disease the animal is inclined to scratch or rub the lesions on any foreign object available; this results in spreading the infective material and causes the lesions to become raw and bleed. Secondary infections are acquired and the original lesions become a most appravated and extended series of skin damages.

"A deposit of pigmented materials (melanins) is often made in the raised part of

the lesion and this causes the lesion to become dark brown or black.

"After becoming fully developed the lesion forms into a scab which later becomes dry and loose and drops off entirely. A very indistinct scar results. If however the lesions become secondarily infected then the resultant scar will vary with the damage done."

Fig. 72 shows the surface of a piece of hog skin infected with hog pox. A group of small lesions has developed into a confluent mass which covers an area of several square inches. The photograph represents the skin reduced ½ in size. Fig. 73 shows a photomicrograph of a cross-section of hog skin cut right through a lesion before the scab had dropped off.

Ringworm Scars

Ringworm is the *athlete's-foot* disease in animals. It is also referred to as *Herpes* and is a contagious skin disease caused by a fungus or mold-like organism. It is described by O'Flaherty and Roddy as follows:

"Ringworm is a very common skin disease of cattle, especially during the winter season, and it is sometimes called barn-itch by the farmer. The mold or fungus causing it is a microscopic sized branching tree-like germ. Spores, which are much like miniature seeds, is the method by which these germs reproduce. Ringworm is spread from animal to animal by direct contact; also by rubbing on infected stalls, walls, and posts.

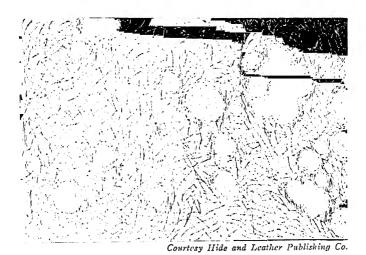


Fig. 74. How the Lesions of Ringworm Remain to Devalue the Finished Leather.

"The germ-molds live in the hair pockets where they cause the hair and its roots to be destroyed, the follicle or pocket becomes inflamed and secondarily infected by other germs which are present in the air. The infection spreads in a circular fashion and results in a loss of hair from round or circular spots. If the infection continues a scar results where each hair pocket was damaged. These run together and finally a large scarred area results. Such areas are usually round varying in size from a pin point to the size of a silver dollar.

"From a clinical standpoint, many distinct forms are recognized—they all scar the

cause the animal to itch and rub, lose weight, and readily contract other skin diseases. This is a direct loss to the owner as the lesions are so evident that the animal does

not bring a good price on the market.

"When the skins or hides have been unhaired, the scars are very evident and the finished leather still shows the scars. The scars appear as bright, shiny spots, the same size as the lesions were during the life of the animal. This leather is lowered in value, yet the cost of the skin to the tanner has been the same as though it were a first grade skin. Secondly, the cost of tanning and finishing such leather has been the same (often times more) as for the production of first class leather, thus resulting in a direct loss to the tanner.

"Ringworm is costly to the live stock industry, and can be readily eliminated. In

this way, a very unjust loss to the leather manufacturer can be avoided."

Warts

Another of the serious economic losses in live stock is a skin disease which produces large masses of wart tissue. This is described by O'Flaherty and Roddy as follows:

"Warts, known technically as verruca vulgaris, are caused by a virus, are thus infectious and the contagion spreads rapidly especially among young cattle. The virus (this is a name for infective material so small in size it cannot be seen under the microscope) is found in the wart-like growth on the skin or in its discharge. When an animal with warts rubs on some object, the object becomes contaminated with the virus and through this and other ways the disease spreads. Calves are most susceptible as warts develop on any part of their body. In adult cattle the warts are more often limited to the head and neck regions.

"Warts are of several varieties-some are soft, break down easily and have a

nasty discharge. Other varieties are hard and almost horn like in character.

"When cattle have warts they show very little general disturbance yet such growths are supported by the animal and cost the live stock owner money. Cattle with warts are unprofitable to the owner for their market value is greatly reduced by their very appearance.

"When warts break off they leave exposed and bleeding skin areas. These are subject to infection by the ever present disease germs and abscesses and other undesirable

conditions result.

"While no actual knowledge is available as to the influence of this disease on the meat, the very sight of an animal covered with warts reduces its market value. The hides are proportionately reduced in value for when warts are numerous it means that an otherwise valuable hide is sacrificed for glue or fertilizer.

"Hides at 10 cents per lb, are worth \$200,00 per ton the best fertilizer can be bought for \$10.00 per ton-this gives one an idea of how reduced in value a hide may become. If only a few warts are present they may be trimmed off but frequently hard warts have injured tannery machinery because of their hard unvielding nature.

"Wart damage is not confined to the skin surface, it affects the entire thickness of

a hide making the leather from such area of little value. Skins and hides with warts are always covered with more germ life than a hide without warts. This means a poorer cure and the introduction of germs into the soak and wash waters. During liming the warts become loose and parts come off in the line. After unhairing a scar results

in all those areas where warts were present.

"After tanning and finishing the damage is still very apparent and the leather is

devalued accordingly.

"So here we see another serious economic loss visited upon the live stock industry effecting further losses in the meat and leather industries. The remedy rests with the live stock industry. This disease can be eliminated by getting rid of all infected animals and by hygienic control of the quarters of the live stock."

The foregoing treatment of the subject of damages occurring on living animals is far from complete, but limitations of space prevent us from attempting a much fuller treatment. However, what has been given will provide tanners with a good start toward a better understanding of many of the damages found on hides and skins as they reach the tannery.

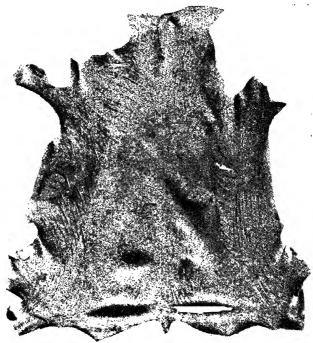
DAMAGES OCCURRING AFTER KILLING

Of the damaged country hides and skins received at the tanneries, the more serious damages may be attributed to lack of experience and skill in flaying, curing and handling the stock preparatory to shipping it to the tanneries, or to downright carelessness and indifference in the work. Big-packer hides command a substantial premium over country hides simply because of the more efficient manner in which the work following the killing is done.

Butcher Cuts

Flaying Damages

In removing the hide from the carcass after slaughter, an inexperienced or careless butcher can completely ruin a hide for purposes of leather manufacture. Fig. 75 shows the flesh side of a hide badly damaged in flaying. Because of the lack of expert use of his knife, the butcher has made a large number of cuts into the hide, which appear as long furroughs or scores or as cuts right through the hide.



Courtesy Hide and Leather Publishing Co.

Fig. 75. Hide Badly Damaged by Poor Takeoff, Butcher Cuts and Scores.

Fortunately, damages of this kind can be seen by the tanner when he buys the hides and he can make claims against such damages, but enormous number of hides are ruined in this way annually.

Poor Pattern

Fig. 46 of Chapter 2 shows the correct pattern, or outline, of a standard bigpacker bide. It is very important to the tanner making good leather that the hide be cut and removed from the animal so that its contour is that of the standard pattern. But this requires skill and care in all the operations of flaying.

Grain Cracks

In the big packing plants, the hide is *pulled* from the beef of the carcass while the *fellbeaters* beat the hide on the flesh side with the backs of cleavers. In some smaller establishments, a workman may use a mallet to assist in removing the hide. Heavy hides can withstand this pounding without serious harm, but calfskins are thinner and the pounding often causes the grain surface to crack. Typical grain cracks on calf leather caused by the use of the mallet in flaying are shown in Fig. 76.



Courtesy Dr. F. O'Flaherty

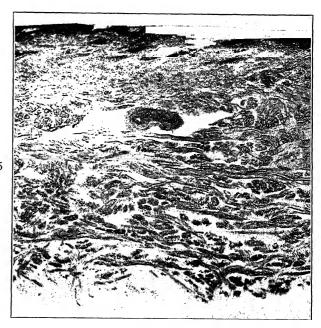
Fig. 76. Grain Cracks on Calf Leather Caused by the Use of the Mallet in Flaying.

Salt Stains

Curing Damages

When green, salted hides and skins are unhaired, they are frequently found to be badly stained with a greenish-blue or rusty-brown color. Usually these stains can be removed by pickling the stock with sulfuric acid and salt, but often the stains cannot be removed by any simple method known and greatly lower the value of the finished leather. These stains are commonly known as salt stains because it was formerly believed that they were caused by the salt used in curing. It is now known that they result from improper curing, although impurities in the salt used may be responsible for many stains. The percentage of stained skins is usually highest in those countries where pure salt is not sufficiently abundant to permit its use in curing.

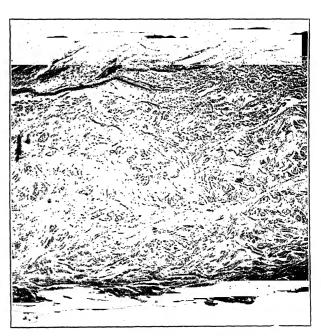
Most salt stains contain iron, which may come from impurities in the salt or from the decomposition of blood left in the hides. If the curing is delayed after



I.ocation:
Belly.
Thickness of section:
40 microns, or 0.0016
inch.
Magnification:
50 diameters.

Fig. 77. Vertical Section of Calf Leather Cut Through Loose Vein.

Location:
Butt.
Thickness of section:
40 microns, or 0.0016
inch.
Magnification:
50 diameters.



Through I once Weir

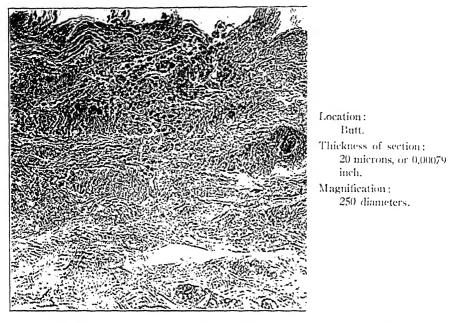


Fig. 79. Vertical Section of Calf Leather Showing Grain Surface Attacked by Bacteria.

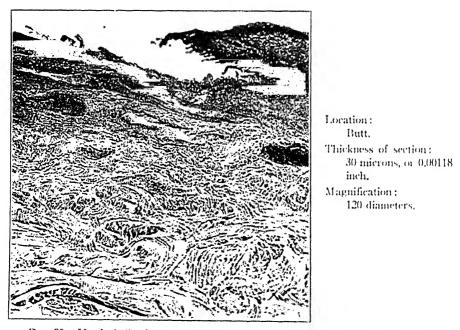


Fig. 80. Vertical Section of Calf Leather Showing Damaged Hair Follicle.

the slaughter, or if decomposition sets in before the stock is completely cured, the percentage of stains is greatly increased. The work of McLaughlin and Theis, described in Chapter 2, shows that the proportion of stains can be reduced by 90 percent simply by washing the stock free from most of the blood immediately after flaying, and then brining and curing.

Paessler found that the percentage of stains could be greatly reduced by using salt to which was added 3 percent by weight of soda ash. The soda ash produces an alkaline condition unfavorable to bacterial action and it tends to precipitate iron salts so that they cannot combine with the hide.

Location:
Backbone.
Thickness of section:
30 microns, or 0.00118
inch.
Magnification:

50 diameters.

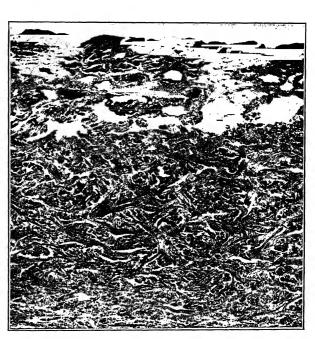


Fig. 81. Vertical Section of Calf Leather Showing Bacterial Damage in Sweat-Gland Area.

Bacterial and Putrefactive Damages

Until fresh hides and skins are properly cured, they are readily putrescible, and every delay in curing after the slaughter adds its toll in bacterial damage to the stock. The penetration of hides by salt is greatly retarded by improper flaying, by coagulated blood, and by changes in the hide that increase with time after slaughter. Those parts of the hide not penetrated by salt are subject to bacterial action until reached by the salt. Often the bacteria will develop along the blood-vessel systems, causing the hide fibers in the vicinities of blood vessels to be destroyed. This results in rather large, open channels following the patterns of the blood-vessel systems and leather produced from such stock is said by the tanner to be veiny. Fig. 77 shows a cross-section of veiny calf leather cut at right angles to the direction of a vein. It will be noted that the hide fibers have been eaten away over an area twice as great as the cross-section area of the vein. Fig. 78 shows a similar cross-section of calf leather cut parallel to the vein.

Fig. 79 shows a cross-section of calf leather in which the grain surface has been attacked by bacteria. Fig. 80 shows another in which the follicle has been attacked and Fig. 81 another in which the bacterial damage has been great in the area of the sweat glands, causing the leather to be loose and pipey.

Shipping Damages

Scratches and Abrasions

Even after raw stock is properly cured and bundled, it may still suffer damage before it reaches the tanner. Where the hides are bundled with the hair side out, careless handling may result in scratches, abrasions and even punctures.

Wetting

If the stock in shipment is allowed to get wet by contact with water, bacterial action will begin again wherever much salt is removed. In the case of pickled sheep skins, the removal of salt will cause an acid swelling with much destruction of the skin fibers.

Overheating

Either green, salted stock or pickled stock may be kept for several years at a temperature of about 60°F., but at temperatures above 90°F., decomposition increases at a very great rate. In very hot weather, it is advisable to ship stock in refrigerated cars and to remove it to a cool place immediately upon arrival at the tannery.

Localized Drying

If stock is not handled properly in transit, there is great danger of partial drying of exposed areas. While this is not damaging in itself, the dried areas will not take up water as readily in the soaking at the tannery as the undried areas. Unless the tanner takes special measures to equalize the water content of the stock before it is allowed to enter the tan yards, the resulting unevenness of the tannage will greatly lower the value of the resulting leather.

Contamination

Any goods in transit may be damaged by contact with other materials. When unloading stock received at the tannery, the tanner must be very alert to locate such contaminations and to make the necessary claims for damage before he puts the stock in process.

Guarding Against Losses

Even the brief descriptions of hide damages given above are sufficient to make the layman wonder how a tanner could ever hope to make good leather without taking staggering losses. Actually the tanners' losses due to the types of damages described above are enormous. In order to minimize them, a tanner must become highly experienced in selecting sources and grades of stock to avoid those that will cause him great losses, and he must be able to detect quickly damages on which he may make legitimate claims.

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Chapter 6

Purchasing Hides and Skins

Before a tanner can make leather, he must purchase the necessary materials. The one fundamental material that he must buy is hides or skins. Since this raw stock may cost him more than one-half of the selling price of his leather, he must buy intelligently or face the possibility of heavy loss. Many a tanner owes his success chiefly to his engaging the services of an expert hide buyer who has devoted his life primarily to the intelligent purchasing of hides for tanners' requirements. Some of the world's largest tanneries have been thrown into bankruptcy by a temporary loss of conservatism in the buying of hides during periods of large market fluctuations. An unusually large element of gambling is forced upon the tanner by the fact that the demand for leather does not influence the production of hides, but merely their market value. Hides are a by-product of the meat-packing industry and become available only in accordance with the demand for meat, and practically all hides made available are tanned into leather. In this chapter, we cannot hope to do much more than indicate the mechanism involved in purchasing hides and skins, their sources and suitabilities for making different types of leathers and methods of reducing the element of gambling to a minimum.

The Producer

A producer of hides is simply an individual or a company that comes into possession of animals, slaughters and flays them and offers the hides for sale. At one extreme, we have the individual farmer who kills one of his animals to get meat for his own family. He may flay the animal and preserve the hide as well as he can until he can get it to a collector of hides or a dealer who will pay him for it. At the other extreme, we have the big packer who slaughters enormous numbers of animals and flays and cures them in a highly efficient manner. Between the two extremes, we have the small packer and the city and country butchers. All are producers, and from them come the raw hides and skins that ultimately are sold to the tanners. A packer may sell directly to a tanner or through the agency of brokers, dealers and the Hide Exchange (Commodity Exchange, Inc. in the United States). As it would hardly be practical for a farmer or other very small producer to offer a hide or two at a time to a tanner, he usually sells to a collector, who gathers enough together to sell to a dealer.

The Collector

A collector contacts many small producers over a given area, buys their hides and skins from them and resells them to a larger dealer. He may merely act as agent for a dealer, or he may be a small dealer himself, selecting, assorting and recurring the stock and offering it for sale to nearby tanners.

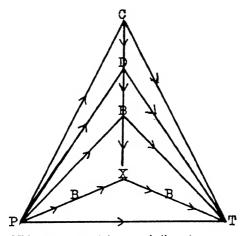
The Dealer

A dealer purchases his hides and skins where he may, from collectors, other dealers or from the producers themselves. His business may vary in size from

little more than that of a collector to one of enormous proportions. He may have agents all over the country and also in many foreign countries. He may specialize only in certain types of raw stock. He may act as agent for dealers in foreign countries. He may have facilities for grading and curing raw stock and usually sells directly to the tanner or to other dealers. He may sell through brokers.

The Broker

The broker serves the tanner in much the same manner as an investment counsel or stock broker does an investor. He is usually an expert hide buyer and advises tanners where to buy hides and skins to the best advantage for their purposes. The more important brokers have offices also in the principal hide centers of foreign countries. The broker makes purchases directly for a tanner's account, charging a stipulated commission for his services. When a tanner does not have an expert hide buyer, it is usually the part of wisdom for him to consult a good hide broker, who specializes in the types of raw stock that he needs for his purpose.



Hides may travel by any indicated route:

Fig. 82. Ways in Which Hides May Pass in Going from Producer to Tanner.

It often becomes advisable for a hide broker to become also a dealer, because he frequently finds opportunities for making very advantageous purchases or sales, which benefit both himself and his tanner clients. A tanner often engages the services of his broker to make purchases directly from a producer, because the broker is more intimately familiar with the market fluctuations and can usually do better for the tanner than the tanner can do for himself.

A tanner also engages the services of a broker whenever he desires to purchase through the Hide Exchange or at the Public Auctions in foreign countries.

Fig. 82 shows the various routes along which the ownership of hides and skins

may travel from the producer to the tanner. The tanner may buy directly from producer, collector, dealer or broker or through the combinations shown.

Hide Prices

No one working in the leather industry should ever lose sight of the fact that hides are a by-product of the meat-packing industry and that the production of hides bears no relation to the demand for leather. An increasing demand for leather increases hide prices, but does not increase the production of hides, whereas an increasing demand for meat lowers hide prices because it results in a greater production of hides regardless of the demand for leather; all hides made available are eventually tanned into leather.

In calculating the cost of the finished leather, it would usually be found that the cost of the raw hide exceeds the sum of all other costs combined, including those of other materials, labor, overhead, etc. Thus, over any extended period, leather prices must rise and fall with hide prices.

When the production of the raw material of an industry is not governed by the demand for the ultimate product, prices of that raw material are naturally subject to enormous variations. Table 19, taken from Price's book, "North American

Table 19. Variaion in Market Price (in cents per pound) of Packer Light Native Cow Hides from January 1909 to August, 1940, Inclusive.

					•	•							
Year	Jan.	Feb.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Direc.	Yearly
1909	13.50	13.50	13.00	13.00	14.25	14.75	15.75	15.75	15.75	16.00	16,00	15.75	14.75
1910	15.00	14.00	13.00	13.50	13.75	13.50	11.50	12.75	13.50	13.50	12.50	11.50	13.17
1911	11.25	11.50	11.50	11.62	12.00	14.00	15.50	14.75	14.75	15.00	15.00	15.00	13.49
1912	14.50	14.50	14.50	14.75	15.50	16.25	16,50	16.34	17.50	17.75	17.75	17.50	10.15
1913	16.75	16.50	16.25	16.00	16.00	16.50	16.75	17.75	18,00	18.50	18.50	18,25	17.15
1914	17.25	17.50	18.50	18.25	19.00	19.00	19.25	19.25	20.00	19.50	20,00	22.00	19.12
1915	23.00	23.50	22.50	19.00	20.00	23.00	25.00	26.00	24.00	23.00	23.00	22,50	22.87
1916	20.00	22,00	21.50	21.50	23.50	24.50	25.00	25.00	24.50	25.50	28,50	32.00	24.46
1917	31.50	30.50	30.00	28.00	31.00	32.00	33.00	32.00	28.00	26.00	28.50	28,00	29.88
1918	25.00	21.00	19.00	16.00	21.00	26.00	26.00	24.00	24.00	24.00	23.00	23.00	22.67
1919	22.00	22.00	23.00	24.00	32.00	37.00	45.00	61.00	50.00	50.00	47.00	43,00	38.1.2
1920	36.00	41.00	35.00	35.00	36.00	34.00	30.00	27.00	25,00	24.50	16.00	15.00	20.54
1921	13.00	12.00	10.00	7.00	8.00	10.00	11.00	12.00	12.00	12.25	12.75	13.50	11.13
1922	13.50	13.50	11.00	10.00	12.25	13.75	15.25	18.50	19,00	19.00	18.50	16.00	15.02
1923	15.00	15.00	15.00	14.25	14.50	14.00	10.50	13.00	11.50	12.25	10.50	10,00	12.96
1924	11.00	11.50	10.00	9.75	9.50	10.50	10.00	13.50	14.00	14.75	15.00	15.50	12.08
1925	14.75	15.25	14.00	13.25	13.50	13.75	15.50	16.00	15.50	15.25	15.00	14.00	14.65
1926	13.75	11.50	12.00	11.00	12.00	13.50	12.50	14.50	14.00	14.50	14,00	13.50	13.06
1927	13.75	13.50	13.00	14.50	16.00	20.00	21.00	22.50	22.00	21.50	21.00	22.00	18.40
1928	23.50	24.00	22.00	25.00	24.50	22.50	22.50	23.00	22.50	19.50	18.50	19.50	22.25
1929	19.00	15.00	14.00	15.00	15.00	15.50	17.00	17.00	17.50	16.50	15.50	13.50	15.87
1930	13.50	13.00	12.50	-12.50	12.50	13.00	13.00	11.00	11,00	11.00	9.50	9,00	11.79
1931	7.50	7.00	9.25	8.50	8.20	10.00	11.75	10.65	2.63	6.80	7.44	7.10	8.49
1932	6.83	6.00	5.88	4.63	4.25	4.25	4.63	6.35	7.75	5.85	6.00	5.00	5.62
1933	5.13	4.63	5.47	6.28	10.19	12.13	13.20	13.75	12.10	9.13	9.75	10,00	9,40
1934	10.13	10.25	9.40	10.89	9.75	9.10	8.69	6.83	7.13	6.88	7.06	8.35	8.76
1935	8.63	8.53	7.93	9.00	10.06	9.85	10.00	10.09	11.00	12.06	11.50	11.31	10,00
1936	11.56	10.63	10.63	10.84	10.58	11.34	10.73	11.05	11.66	11.75	12.97	13.75	11.46
1937	14.25	13.99	15.38	15.83	15.40	15.15	15.88	17.25	17.00	13.50	11.50	10,60	14.64
1938 1939	9.63	8.55	8,66	8.45	8.75	8.75	10.65	11.42	11.03	12.49	12.79	11.42	10.22
1939	10.64	10.13 12.97	10.68 12.71	9.31	10.17	11.00	11.25	11.12	15.14	15.62	13.99	14.64	11.97
13.40	13.65	12.97	12./1	12.88	12.63	10.38	11.88	10.17			• • • •		

Prices shown for years to and including 1930 represent selling price at the first of the month, as compiled in *Pratt's Manual*; subsequent years represent weekly selling price averaged for the month, as compiled by the Commodity Exchange, Inc., New York.

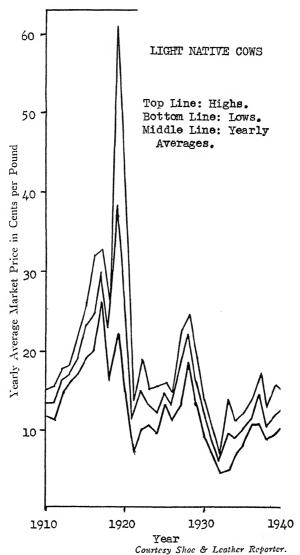


Fig. 83. Variation in Market Price of Packer Light Native Cow Hides by Years from 1910 to 1940.

Packer Hides," page 71, shows how the market price of packer light native cow hides has varied from 1909 to 1940.

For convenience in study, the yearly averages have been plotted to make the graph shown in Fig. 83, together with the highest and lowest monthly value for each year shown in the table. It should be remembered that the high and low values do not represent the extremes for individual sales, but only the high and low monthly values for each year, as described at the foot of the table.

Although it is interesting to study the effects of the World War and the subsequent depressions on hide prices, the relation is not simple because of the marked effects of speculation and other causes.

SPECULATION

The making of leather is a highly competitive business, and fortunate indeed is the tanner who can average a net profit of 5 percent of the selling price of his leather. Before a tanner can make leather to sell, he must buy the hides. It may require from a month to a year to convert the hides into salable leather, and he must expect to sell the leather based on the price of hides at the time the sale is made. If hide prices drop considerably during the period required for the tanner to convert the hides he has purchased into salable leather, he may be confronted with the necessity of selling the leather at a heavy loss. If hide prices rise during this period, he may hope for an extra profit to offset losses sustained during a period of falling prices, but he is more likely to find some of his competitors offering leather based on the prices at which they bought their hides.

Sound business is not based on speculation, but the purchase of hides is of necessity always a speculative venture. Fortunately, there are ways of minimizing speculation in hides, and every tanner should become intimately familiar with them. As long as a tanner owns either hides or leather, he must accept the risk of a varying hide market. In order to eliminate this risk, he must avoid virtual ovenership. There are at least three ways in which this can be done.

Avoiding Speculation by Buying Hides When Selling the Leather

Some manufacturers of leather goods make their purchases of leather chiefly only at certain seasons and well in advance of their needs for actual delivery. They must know the price of the leather before placing the order so that they can calculate the cost of their goods before manufacture is started, and they must order far enough in advance to insure prompt deliveries as the leather is needed. Since competing manufacturers must follow the same procedure, the result is that the selling prices of the goods are established long before the goods are manufactured and no longer subject to change for the particular season involved by any subsequent variation in the hide market.

The tanner bases the price of the leather on the hide market of the day the order is accepted and purchases the hides to fill the order on that day. From the moment of purchase of the hides, virtual ownership rests with the customer whose order the tanner has accepted, and the tanner escapes all risk involved in the fluctuating hide market.

Although the United States Government and many manufacturers of such goods as luggage and sporting goods often buy their leather in this manner, most leather cannot be sold until after it has been made. Therefore, tanners must usually resort to other methods of avoiding virtual ovenership of hides.

Avoiding Speculation by Contract Tanning

There are some manufacturers of leather goods who find it to their own advantage to purchase the hides themselves that are to be converted into the types of leather they desire. They then engage the services of tanners to convert the hides into leather. Although this practice involves only a relatively small proportion of the total leather manufactured, many tanners take advantage of it as a means of avoiding ownership of hides and the risks involved.

Avoiding Speculation by Hedging

For most of the leather produced, the tanner must buy hides and convert them into leather before he can effect a sale. However, just as soon as he buys hides to manufacture into leather to be sold at some future time, he has speculated on the trend of hide prices; he has bet that hide prices will remain stationary or will rise. *Hedging* is betting so as to offset a bet already made. In order to avoid speculation, having made his bet by buying hides, he must simultaneously hedge by selling an equivalent amount of hides for delivery at the time he sells his leather. He does not sell the hides with any intention of making physical delivery. The Hide Exchange provides him with the means of making and discharging contracts without involving the physical exchange of hides.

Physical possession and virtual ownership of hides are two very different things. Physical possession is an obvious necessity for anyone desiring to make leather, but virtual ownership carries with it the gamble of a fluctuating hide market. When a tanner buys hides, he acquires both, but the Hide Exchange provides him with the means for retaining physical possession and selling the virtual ownership. The speculators want virtual ownership, because in that resides the gamble, but they do not want physical possession, because they do not make leather.

By keeping future contracts sold to the value of both raw stock and leather in his possession, a tanner can not only eliminate the gamble of a fluctuating hide market, but he can actually make an assured profit that may be greater than all other profits in his business combined. The detailed mechanism of the tanner's selling of hide futures as a hedge will be discussed later in this chapter, following the presentation of the Hide By-Laws and Rules of Commodity Exchange, Inc.

Any exchange on which trading is done in stocks or commodities with fluctuating values is a temptation to the gambler, and the Hide Exchange is no exception. Although tanners buy hides because they must have physical possession of them to make leather, many speculators, who have no interest in the possession of hides to make leather, buy hide-futures contracts on the Exchange solely for the profit they hope to make. Speculation in any commodity is bound to affect its market price, and the lure of the Hide Exchange to the speculator with no direct interest in hides is very great. Many tanners, particularly those not intimately familiar with futures trading, have told the writer that they regard the Hide Exchange as harmful to their interests because it invites speculation in a commodity whose market-price variation is already too great to permit tanners to operate their businesses with reasonable safety. On the other hand, tanners who make continuous use of hedging have told the writer that they consider the Hide Exchange essential to them in climinating or greatly reducing the elements of speculation. If the only way for the tanner to escape the speculative risks of a varying hide market is to avoid virtual ownership of hides, then a system which provides him with the means for shifting the risk to others is worthy of his most careful study, even though those who accept the risk may do so in the hope of ultimate profit.

Spot and Futures Trading

When hides are bought and sold by private transactions involving specific lots and grades of hides sold for a definite delivery date, the procedure is known as *spot* or *cash trading*. Where trading is done on an organized market through the buying and selling of *standard contracts* which call for the future delivery of the hides, the procedure is known as *futures trading*. Futures contracts are the same

for all traders; each describes the unit of quantity, the grade or grades which are deliverable and the place or places where and the method by which delivery shall be made. Only the determination of the month of delivery and the price are left open to the contracting parties. The difference between spot and futures markets is not one of time of delivery; hides may be bought or sold in the spot market for delivery several months into the future, while a transaction in the futures market may call for delivery during the current month. The Hide Exchange is exclusively a futures market.

Commodity Exchange, Inc.

In 1933, the New York Hide Exchange consolidated with other exchanges dealing in metals, rubber and silk to form Commodity Exchange, Inc., a New York corporation, serving as a national exchange. The trading floor is located at 81



Fig. 84. Trading at the Hide Ring on Commodity Exchange, Inc., September 1, 1939.

Broad Street in the City of New York. A picture of hide brokers trading in futures at the Hide Ring on Commodity Exchange, Inc., is shown in Fig. 84. The division of Commodity Exchange, Inc. relating to hides is still generally referred to as the Hide Exchange, and we shall use the name in that sense.

Although the Hide Exchange deals only with domestic steer and cow hides and with Frigorifico hides from South America, it is used for hedging purposes by tanners of all kinds of stock on the theory that major rises and falls in market prices carry with them all classes of raw stock.

The hide by-laws and rules contain so much important information that every tanner should know that they are reprinted here in full with the permission of Commodity Exchange, Inc. The reader's attention is called to the fact that they are subject to change by amendment from time to time when conditions require. The text of the By-Laws and Rules, as it now stands (July 23, 1940), contains provisions governing the *old contract*, which was superseded by the *new contract*; the provisions relating to the old contract will probably be deleted when the occasion arises.

Hide By-Laws

Hide Trade Committees

Sec. 801.* Pursuant to Section 123 of the By-Laws, the following Standing and Revolving Committees shall be appointed by the Board Hide Trade Group:

1. Committee on Quotations for Hides.

2. Committee on Grading and Warehousing for Hides.

Committee on Quotations for Hides

Sec. 802. The Committee on Quotations for Hides shall consist of five registered members of the Hide and/or Non-Trade Group of the Exchange, one of whom shall retire at the end of each month. It shall report to the Secretary the tone and price of the contract market in hides. It shall meet each day, at the close of the Exchange, and by a majority vote determine the closing quotations for contracts for future delivery and report them to the Secretary. It shall have authority to establish quotations for any months in which few or no transactions may have occurred during the Exchange hours of that day, and in so doing it shall take into consideration the fluctuations in other months during the day and fix the price in harmonious relation thereto.

Committee on Grading and Warehousing for Hides

Sec. 803.† The Committee on Grading and Warehousing for Hides shall consist of thirteen registered members of the Hide Trade Group at least one of whom shall be a member of the Board Hide Trade Group and the Chairman of the Committee. Four members of the Committee shall constitute a quorum. For the hearing of appeals as provided in Section 808 of these By-Laws, a quorum of the Committee shall consist of five members, but in the absence of members essential to constitute a quorum for this purpose, the Vice-President of the Hide Trade Group, or in his absence the President of the Exchange, may appoint registered members of the Hide Trade Group as additional members of the Committee pro tem for service on the hearing of a particular appeal only.

members of the Committee pro tem for service on the hearing of a particular appeal only.

The Committee shall maintain an Inspection Bureau to consist of the Inspector-inChief and such other persons as the Committee shall designate. The Committee shall have general supervision over and direction of the Inspection Bureau, subject to the

Board Hide Trade Group.

The Committee shall investigate all applications for licenses filed by warehouses, weighers and employees of the Inspection Bureau, and it shall also investigate all complaints against licensed warehouses, weighers and employees of the Inspection Bureau and make its recommendations to the Board Hide Trade Group in respect thereto.

The Committee shall have the power to make suitable arrangements for the ware-housing of certificated hides and to require the maintenance of proper facilities therefor.

The Committee shall submit to the Board Hide Trade Group for its approval the names of plants producing Frigorifico hides to be placed on or removed from the official list, as provided for in Section 825 of these By-Laws.

The Committee shall have power subject to the approval of not less than three members of the Board Hide Trade Group to formulate such regulations, pursuant to the By-Laws, for the guidance of the Inspector-in-Chief and his employees, and for licensed warehouses and licensed weighmasters, and in respect to the inspection, warehousing and delivery of hides as in its opinion may be desirable or necessary.

Any request for a ruling or interpretation of the By-Laws, Rules and Regulations relating to matters incident to the hide contract shall be referred to the Committee,

^{*} Amended Nov. 28, 1933, June 1, 1935.

[†] Amended April 2, 1934.

which shall formulate its ruling or interpretation subject to the approval of the Board Hide Trade Group and adoption by the Board as a whole.

The Committee shall have such other powers as are conferred upon it by the By-Laws, Rules and Regulations of the Exchange, the Board Hide Trade Group, or by the Board as a whole.

Inspector-in-Chief for Hides

SEC. 804. The Board Hide Trade Group on recommendation of the Committee on Grading and Warchousing for Hides, shall appoint an Inspector-in-Chief for hides. The Committee on Grading and Warchousing may appoint an Assistant Inspector-in-Chief, subject, however, to the approval of the Board Hide Trade Group.

When called upon to make an inspection of hides, the Inspection Bureau shall assign an Inspector and a licensed weighmaster to proceed with the inspection and weighing of the hides. There shall be kept a record of all hides inspected, of the marks under which they are submitted, re-marks, classification, weights and the month (or months) of take-off and date of removal from salt pack, and a record of the name or names of person or persons by whom the hides were inspected and weighed, the place and date of inspection and weighing, the inspection numbers, names of parties requesting inspection, store numbers and all other necessary details and also the determination of the discount, if any, from standard of the lots inspected for certification for delivery against the hide contracts.*

When called upon to make an inspection of hides, the Inspection Bureau may require the party offering the hides for certification to submit a complete history of the hides, the pack from which they are taken, and any other data which the Inspection Bureau deems necessary. If the data furnished is not satisfactory, the Inspection Bureau may refuse to certify the hides.

The Inspector-in-Chief may appoint, subject to the approval of the Committee on Grading and Warehousing and of the Board Hide Trade Group, inspectors and such other employees as he may deem requisite. The salaries of all employees shall be fixed by the Board as a whole.

The duties of the Inspector-in-Chief may be performed by the Assistant Inspector-in-Chief or any other person authorized by the Board Hide Trade Group.

Request for Certification of Hides

SEC. 805.† (a) Any member of the Exchange desiring the inspection of hides for certification, shall notify the Inspection Bureau in writing, stating the number of hides, the location thereof (which place must be a licensed warehouse) the grade, the marks or identification thereon, if any, the plant of origin, the month or months of take off, the opening and closing dates of the pack, the date or dates when said hides were removed from the original pack and the date when same will be at the warehouse ready for inspection and such other information required by these By-Laws, Rules, Regulations and the Inspection Bureau. Such notices shall be lodged with the necessary documents in the office of the Inspection Bureau not later than three o'clock on the second business day preceding the day for which the inspection is requested.

(b) The member desiring certification shall deliver to the Inspection Bureau such documents as said Bureau may require.

(c) After receiving a request for the certification of hides, the Inspection Bureau, shall, as soon as possible, cause said hides to be inspected and to be weighted provided that all requirements have been fulfilled to the satisfaction of the Inspection Bureau. When a request for certification and/or documents have not been presented to the Inspection Bureau in satisfactory form, the Inspection Bureau may at its discretion return the request for certification.

(d) The Inspection Bureau shall not be liable for any delay in the inspection and certification of hides.

(e) If for any cause whatsoever the hides to be inspected are not ready for inspection on the date designated in the request for certification, the owner of the hides shall be liable to the Inspection Bureau for the loss, if any, caused by the delay. The Inspection Bureau shall report such cases to the Committee on Grading and Warehousing which shall determine and assess the amount of money due and require its payment.

^{*} Amended April 2, 1934, Aug. 1, 1938,

[†] Amended April 2, 1934, June 1, 1935.

Certification of Hides

Sec. 806. From the inspection made by the Inspection Burcau and/or from the data at hand, the Inspection Bureau shall determine if the hides submitted are eligible for certification. No hides shall be eligible for certification which are not properly declared in the request for certification. The Inspection Bureau shall determine such factors as are required by the By-Laws, Rules and Regulations in connection with the certification of hides. As soon as practicable after the inspection and weighing of the hides is completed, the Inspection Bureau shall, if the hides are eligible for certification, issue hide certificate in the form approved by the Board Hide Trade Group. The hide certificate shall be signed by the Inspector-in-Chief, or any other person designated by the Board Hide Trade Group.

Rc-Certification of Hides

Sec. 807.* Hides which have been certificated may be submitted for recertification and subsequent successive recertifications as provided in the By-Laws, Rules and Regulations.

A member tendering hides for recertification shall, not later than the second business day after the expiration of the hide certificate, present to the Inspection Bureau a request in writing for recertification and an inspection order, and shall surrender to the Bureau

the hide certificate.

The Inspection Bureau shall, as soon as feasible, cause hides tendered for recertification to be inspected in accordance with such regulations as may be adopted with respect thereto. The Inspection Bureau shall not be liable for any delay in the inspection or

recertification of hides.

If hides are found eligible for recertification, in accordance with the By-Laws, Rules and Regulations relating thereto, the original certificate shall be endorsed, or a new certificate shall be issued, as may be provided by regulation, and such endorsement or new certificate shall extend the life of the hide certificate from the date of examination of the hides for such recertification until the end of the twelfth month following that in which said examination occurs, provided, however, that if the examination does not take place until after the date of expiration of the hide certificate, the life thereof shall be extended for one year from said date of expiration.

If hides tendered for recertification are not eligible therefor, the certificate shall be cancelled by the Inspection Bureau. A member whose request for recertification has been denied shall have the right of review inspection, and appeal, as provided in Section 808

of the By-Laws, and the Rules and Regulations.

The charge† for recertification of hides shall be Fifteen Dollars (\$15.00) per contract unit, subject to change by the Board in its discretion. Said charge shall be paid by the party requesting recertification and in accordance with the provisions of Section 811 of the By-Laws relating to original certification, and no part of said charge shall be passed on to the receiver on an Exchange contract.

Appeal from Determination of the Hide Inspection Bureau

SEC. 808. If the person offering the hides for certification is dissatisfied with the determination of the Inspection Bureau in any respect, he may within four (4) business days following the receipt of the determination of the Inspection Bureau, appeal to the Committee on Grading and Warehousing by filing written application therefor with the Secretary of the Exchange. Said Committee shall hear said appeal as provided in Section 803. If the Committee deems it advisable, it shall cause another inspection of the hides to be made by practical hide inspectors, who are not directly or indirectly interested in the matter, and the Committee shall thereupon make its findings accordingly. Upon such an appeal, no member of the Committee on Grading and Warehousing shall participate who has any interest directly or indirectly in respect thereto. The Committee on Grading and Warehousing * may affirm, modify, after or reverse any finding or determination of the Inspection Bureau and may thereafter make its own determination in respect to any matter involved in the appeal. The determination of the Committee on Grading and Warehousing shall be final.

The Committee on Grading and Warehousing shall determine what costs, in addition to the actual disbursements which have been incurred, shall be borne by the appellant,

* Adopted June 1, 1935. Amended Aug. 1, 1938.

[†] Charge increased from \$15.00 to \$25.00 Jan. 21, 1938. Charge reduced from \$25.00 to \$15.00 Aug. 1, 1938.

[#] Amended April 2, 1934.

said costs, however, not to be less than \$60.00, nor more than \$100.00 per contract unit. If on the appeal it develops that the Inspection Bureau erred to the disadvantage of the owner of the hides, no charge shall be made against the appellant for the appeal.

Inspection, Grading and Weighing of Hides

SEC. 809. The inspection, grading and weighing of hides shall be subject to and done in accordance with the By-Laws, Rules and Regulations of the Exchange in force at the time of such inspection and weighing.

Validated Notice on Delayed Certification or Re-Certification

SEC. 810.† If, upon the date fixed for delivery in the transferable notice, Hide certificate shall not have been issued, or in the case of recertification, endorsement shall not have been made or new certificate shall not have been issued by the Inspection Bureau for the lot of hides to be delivered pursuant to such transferable notice, the delivery of such lot of hides may be made upon compliance with and subject to the following conditions.

In the case of original certification, such hides shall have been delivered to the ware-house and in readiness for inspection not later than three o'clock p. m. the second business are properly tendered to the Inspection Bureau for certification; and in the case of recertification, the request for recertification shall have been made to the Inspection Bureau within the time and in the

manner prescribed by the By-Laws, Rules and Regulations.

If on the morning of the delivery day specified in the transferable notice the hide certificate covering the hides involved is not ready for delivery when called for, the tenderer of the hides shall present to the Inspection Bureau a written notice stating to the best of his knowledge and belief the true grade and quality of each individual lot to be delivered. If the foregoing requirements shall have been complied with, the Inspection Bureau shall cause to be written or stamped on such written notice a statement validating it for use in the tender only on the specified delivery day of the hides covered thereby pending the issuance of hide certificate in accordance with these By-Laws. The tenderer shall, on the specified delivery day, deliver such notice to the receiver of the hides, together with the warehouse receipts and such other papers as may be necessary to the delivery of the hides on such day.

The member making the tender shall deliver the covering hide certificate to the receiver of the hides before the close of business hours on the day following the date

of the issuance thereof.

Charges for Certification of Hides

SEC. 811.* The charge for inspection and certification of hides shall be Thirty Dollars (\$30.00) per contract unit for the initial inspection and certification of hides; but in addition thereto the Inspection Bureau may impose additional charges under such circumstances as may be provided for by regulations.

Where a request for certification is withdrawn before the Inspection Bureau has commenced the inspection of the hides, a charge of \$10.00 shall be made; in all other cases, where a request for certification has been made, the full charge provided for in

the preceding paragraph hereof shall be imposed.

The charges herein provided may be varied from time to time by the Board.

The Inspection Bureau shall render monthly bills to the member at whose request said services were rendered, and shall furnish duplicates thereof to the Treasurer of the Exchange. Any failure to pay the amount billed within one week from the date on which the bill was rendered shall be reported to the Supervisory Committee.

The Inspection Bureau shall collect and turn over to the Treasurer of the Exchange all sums collected under this Section and the Treasurer shall keep a separate account

thereof.

Provisions in Respect to Hide Certificates

Sec.[‡] On hides which are eligible for certification:

(1) The initial life of the Hide certificate shall run for a period of two years from date of removal of the hides from original salt pack, and shall continue thereafter until the last day of the month in which the date of expiration falls. (In the case of "South

[†] Amended Aug. 1, 1938.

^{*} Amended Aug. 1, 1938. Charge reduced from \$60,00 to \$30,00 Aug. 1, 1938,

[‡] Adopted April 2, 1934. Amended June 1, 1935, Aug. 1, 1938.

American" hides, removal from original salt pack shall mean original pack in the plant of origin).

(2) The Hide certificate shall be conclusive evidence of the grade, weight and other

factors therein specified until its expiration.

On hides which are eligible for recertification:

(3) The Hide certificate shall be extended by endorsement, or a new certificate for the period of recertification may be issued, as may be provided by the By-Laws, Rules or Regulations.

Exchange of Hide Certificates

SEC. 812A.‡ Certificates which are outstanding at the date of adoption of this provision may, under the following circumstances, be exchanged for the new form of certificate to be issued after the adoption of this provision, and in such cases the applicant for such new certificate shall surrender the outstanding certificate to the Inspection Bureau, which shall make such examination of the hides as it may deem proper:

(1) If, at the date of application for exchange, the hides certificated shall have been out of original salt pack for less than two years from end of month in which they were removed from salt pack, the new certificate to be issued in exchange for the outstanding certificate, shall expire at the end of the twenty-fourth month following that in which the

hides were removed from original salt pack.

(2) If, at the date of application for exchange, the hides shall have been out of salt pack for more than three years from end of month in which they were removed from salt pack, and have been recertificated, the new certificate shall expire at the same time as the old certificate in exchange for which it is issued.

(3) The charge for an exchange of certificates as provided in paragraphs 1 and 2 above shall be \$5.00 per contract unit. Said charge shall be paid by the party requesting the exchange of certificates and no part of said charge shall be passed on to the receiver

on an Exchange contract.

(4) If at the date of application for exchange, the hides shall have been out of original salt pack for more than two but less than three years from end of month in which they were removed from salt pack, an outstanding certificate may be exchanged for a new form of certificate only upon recertification of the hides in accordance with the provisions of Section 807 of the By-Laws, and in such case the new certificate shall expire at the end of the twelfth month following that in which examination for recertification occurs, as provided in said Section.

(5) In any case where hides have been out of original salt pack for more than two years from end of month in which they were removed from salt pack the holder of the outstanding certificate may apply for recertification of the hides pursuant to the provisions of Section 807 of the By-Laws and in such case the new certificate shall expire at the end of the twelfth month following that in which examination for recertification

occurs, as provided in said section.

(6) The Inspection Bureau shall not be responsible for any delay in the issuance of the new form of certificates.

Limitations on Delivery of Certificates against "New" and "Old" Contracts

SEC. 812B.* Hide certificates outstanding at the date of adoption of this provision shall be valid for delivery only against the "Old Standard Contract." Hide certificates issued in the new form after the date of adoption of this provision shall be valid for delivery against either the "Old Standard Contract" or the "New Standard Contract," provided, however, that Hide certificates in the new form shall not be tenderable for delivery against the "Old Standard Contract" if such certificates are for hides which have been out of original salt pack for more than five years from end of month in which they were removed from salt pack, or are for lots of any of the following grades, viz: Native Cows and Steers (all weights); Branded Cows and Steers, (all weights); Pacific Coast Native and Branded Cows; Pacific Coast Native and Branded Steers.

Cancelled Hide Certificates

SEC. 813. If by reason of an appeal it shall be determined that the specifications set forth in the hide certificate shall be changed, such certificate shall be cancelled and there

[#] Adopted Aug. 1, 1938.

^{*} Adopted Aug. 1, 1938.

shall be issued in lieu thereof a new certificate showing the change as determined on such appeal,

Lost Hide Certificates

SEC. 814. Upon the written request of the last holder of a valid hide certificate and a showing to the satisfaction of the Inspector-in-Chief who issued such certificate that it has been lost or destroyed, and, if lost, that diligent effort has been made to find it without success, and upon satisfactory proof to the Inspector-in-Chief that the hides covered by said certificate are in licensed warehouse, a new certificate shall be issued without the re-inspection of the hides. Such new certificate shall bear the same number and date of issuance as the lost or destroyed certificate, and shall include a statement to the effect that it is a duplicate issued in lieu of the lost or destroyed original, as the case may be.

Storage and Transfer of Certificated Hides

SEC. 815. Certificated hides shall be stored only in warehouses, licensed as provided in these By-Laws, and may be transferred from one warehouse to another under

the direction of the Inspection Bureau.

Any hide certificate shall become invalid for use in the tender or delivery of the hides covered thereby whenever such hides shall be removed from the place of storage specified therein, except when it is handled and re-stored or transferred to a different place

of storage under the supervision of the Inspection Bureau.

For purposes of delivery of hides upon contract by warehouse receipts, one warehouse shall be understood to mean a single warehouse; or, a number of contiguous warehouses comprising one system of warehouses under one name or management; or warehouses or systems of warehouses that are in juxtaposition to each other, though bearing different names, when such warehouses are adjoining and contiguous to each other and are all managed or operated by one warehousenant.

Licensed Warehouses for Hides

Sec. 816. Warehouses may be licensed for the storage of hides upon the recommendation of the Committee on Grading and Warehousing and with the approval of the Board Hide Trade Group. The Board Hide Trade Group shall fix the term of the license of all warehouses.

Licensed warehouses shall give such bonds to the Exchange as may be required

by the Board Hide Trade Group.

Each warehouse shall furnish to the Secretary of the Exchange daily a list of all certificated hides delivered to and removed from the warehouse on the previous day.

Warehouse Receipts for Hides

SEC. 817. After the hides have been placed in a licensed wavehouse, negotiable wavehouse receipts stating the lot number, the marks on the hides and the number of hides in the lot shall be immediately issued to their owners. Receipts shall be lettered or numbered consecutively by each wavehouse and no two receipts shall bear the same letter or number. No receipt shall be issued for more than or less than one contract unit.

Licensed Weighmasters for Hides

SEC. 818. Official weighmasters shall be licensed by the Board Hide Trade Group as follows:

Every application shall be addressed to the Board Hide Trade Group and indorsed by two registered members of the Hide Trade Group of the Exchange. Said application shall thereupon be referred by the Board Hide Trade Group to the Committee on Grading and Warehousing, which Committee shall investigate the character, qualifications and responsibility of the applicant and report to the Board Hide Trade Group.

If the application for a license be approved by the Board Hide Trade Group, a license shall be issued, which license shall be signed by the Vice-President of the Board

Hide Trade Group and the Secretary of the Exchange.

Any license issued as above provided may be cancelled by the Board Hide Trade Group at any time, by a notice in writing stating the intention to cancel, given by the Exchange to the weighmaster.

Delivery Points for Hides

SEC, 819. The delivery of hides on Exchange contracts shall be made only from licensed warehouses located in the City of Chicago, Illinois; in the Port of New York; and in addition thereto, at such other delivery points as the Board Hide Trade Group may designate. The designated delivery points may be added to or climinated at the

discretion of the Board Hide Trade Group, subject to the approval of not less than three members of the said Board, after notice to members; said notice shall fix the time when such changes shall become effective for delivery. There shall be no charges or allowances made for freight adjustment on any deliveries.

Definitions and Construction in Respect to Hides

SEC. 820. Whenever used in these By-Laws or Rules, unless the context otherwise requires, the following words and expressions in respect to Hides shall be defined as follows:

CLASS-Wherever referred to in the By-Laws, Rules, or Regulations, the term "class" shall be deemed to include the following: Native and branded steers and cows, Colorado steers, Texas steers, Butt branded steers and Frigorifico steers, Frigorifico light steers, Frigorifico extreme light cows and steers, and Frigorifico cows.

CURED—Put in state of preservation through chemical action of salt.

CUT—An incision through a hide beginning on the flesh side, usually made by a knife in the process of flaying.

Deep Score—A score that may be punctured by a skewer through the hide. Grade—Whenever the word "grade" is used in the By-Laws, Rules, or Regulations, the same shall be understood to be inclusive of class, sub-class and selections.

Score—A slight cut or incision in any part of the hide which does not entirely perforate

SEASONAL PERIOD OF TAKE-OFF—Wherever referred to in the By-Laws, Rules, or Regulations, the term "seasonal period of take-off" shall be deemed to refer to a single month or group of months for which a single differential has been fixed in the By-Laws.

Selection-Wherever referred to in the By-Laws, Rules, or Regulations, the term "selection" shall be deemed to refer to the No. 1 or No. 2 qualities of each class, sub-

class and grade.

SPLECTION FACTORS-Wherever referred to in the By-Laws, Rules, or Regulations, the term "selection factors" shall be deemed to include the characteristics as specified in the last column entitled "Selection Factors" in the tables in the By-Laws.

Sub-Class-Whenever referred to in the By-Laws, Rules or Regulations, the term "subclass" shall be deemed to include the following characteristics: heavy, light, extra light and all weights.

Extension of Credits for Hides

SEC. 821.* The extension of credit to a customer in connection with the purchase and/or sale of Hides on the Exchange when permissible under Section 411 of the General Trading By-Laws, shall not exceed a maximum of \$1,000.00, irrespective of the number of contracts.

Commissions, Floor Brokerage and Charges on Hide Contracts

Sec. 822.† The following rates of Commissions, floor brokerage and charges are the lowest that may be charged on each contract for future delivery of hides:

(a) For members of the Exchange residing within the United States and Canada: Commission for

	Commission	n ror
Based upon a price	Buying or	Selling
Below 10c per pound	\$7.50	
10c per pound and above		

(b) For non-members residing within the United States and Canada double the above rate of commission shall be charged.

(c) For members and non-members residing outside of the United States and Canada, a commission of \$2.50 shall be charged in addition to the above rates.

(d) For each contract bought or sold by one member for another, giving up his

principal on the day of the transaction:

Based upon a price	Buying or Selling
Below 10c per pound	
10c per pound and above	2.00

^{*} Amended Jan. 26, 1940.

[†] Amended April 2, 1934.

(c) Two dollars for each contract bought and sold where one member clears for another member transactions made or initiated during the day by him personally or for his account while present on the floor of the Exchange. No member shall be entitled to the privilege of clearance of contracts for his account, unless the purchase and sale were personally made by him, or the transactions were initiated and the orders both of purchase and sale were given by him while actually present on the floor of the Exchange. The foregoing clearance charge is exclusive of floor brokerage.

(f) Upon the delivery or receipt of hides or when a contract is settled by giving or receiving a transferable notice in fulfillment thereof, a commission shall be charged and paid in addition to that above provided for the purchase or sale of

the hides and shall be not less than said purchase or sale commission.

(g) (Deleted 6/1/36).‡

Hide Contract for Future Delivery

SEC. 823.* All contracts for future delivery of hides shall be in the following form for either the "Old Standard Hide Contract" or the "New Standard Hide Contract."

COMMODITY EXCHANGE, INC. STANDARD HIDE CONTRACT

A. B. have this day bought and agreed to receive from C. D. 40,000 pounds of Wet Salted Hides (5 percent more or less) at the price of cents per pound for Standard No. 1 Light Native Cows-July, August or September take-off, with additions or deductions for other grades and factors, as provided in the By-Laws, Rules and Regulations of Commodity Exchange, Inc., deliverable from licensed warehouse

between the first and last delivery days of inclusive, at the seller's option, upon notice to buyer as provided by the By-Laws, Rules and Regulations of Commodity Exchange, Inc.

Either party may call for a margin, as the variations of the market for like

deliveries may warrant, which margin shall be kept good.

This contract is made in view of, and in all respects subject to the By-Laws, Rules

and Regulations of Commodity Exchange, Inc.

For and in consideration of One Dollar (\$1.00) to the undersigned, in hand paid, receipt whereof is hereby acknowledged, the undersigned accepts this contract with all its obligations and conditions.

Verbal contracts (which shall always be presumed to have been made in the approved form) shall have the same standing, force and effect as written ones, if notice in writing of such contracts shall have been given by one of the parties thereto to the other party during the day on which such contract was made.

Trading in the "New Standard Hide Contract" shall commence at the opening of trading in hides on the first day of August, 1938, and the first delivery month for which contracts may be traded shall be September, 1938.**

In all trades made for the future delivery of hides, members shall specify whether said trades are in respect to the "New Standard Contract" or the "Old Standard

All By-Laws and Rules herein contained relating to hides shall apply to both the "Old Standard Contract" and the "New Standard Contract," unless otherwise specifically provided.

Tenderable Grades of Hides

Sec. 824.† Hides tenderable against Commodity Exchange, Inc., "Old Standard Hide Contract" or "New Standard Hide Contract" shall be certificated under one of the grades enumerated in Section 825, subdivision (9). In each instance the lot offered

[‡] Amended June 1, 1936.

^{*} Adopted April 2, 1934. Amended Aug. 1, 1938.

^{**} Adopted Aug. 1, 1938.

[†] Adopted April 2, 1934. Amended Aug. 1, 1938.

for certification shall be in good, sound merchantable condition, and shall conform to the requirements of the By-Laws, Rules and Regulations of the Exchange relating to the grade of hides tendered.

Specifications for Deliverable Hides

SEC. 825.‡

(1) STANDARD OF QUALITY AND TAKE-OFF

Hides which conform to the standards of quality and take-off maintained by producers employing expert butchers and flayers and which conform to the specifications provided in the By-Laws, Rules and Regulations of the Exchange in respect to flaying, trim, pattern, cuts, scores, selections, curing, grading and delivery, and hides superior to the foregoing, shall be certificated as standard. A contract unit of hides which is inferior to a standard unit of the same grade shall be eligible for certification provided the value of such unit, in the judgment of the Inspection Bureau, is not more than one and one-half cents per pound under the value of a standard unit based upon a fair average market level for hides. In each instance the Inspection Bureau shall indicate on the hide certificate the amount of discount, if any, from standard for the particular lot. The discount from standard shall be determined by the Inspection Bureau in accordance with Regulations that may be adopted from time to time. All questions relating to certification shall be subject to appeal as provided in Sec. 808 of the By-Laws. In the event of any change in the method of determining such discount, such change shall not be deemed to affect the grade or quality of hides to be delivered, or the amount of money to be paid upon outstanding contracts.

(2) ORIGIN

Domestic Hides shall be tenderable only if they have been taken off in establishments in the United States of America, from cattle slaughtered within districts designated by the U. S. Government as "free from ticks" (and including hides produced in Canada of the same character and description). The Inspection Bureau may require documentary proof of origin as a condition for certification. Hides shall be eligible for certification which are the output of one or more cellars (or floors) of one producing plant in a single city, or the take-off of more than one abattoir in a single locality under joint or cooperative arrangements between the producers for salting in a single cellar in collective packs in an original run as to their collection from each producer. Such cooperative arrangements shall be subject to the approval of the Committee on Grading and Warehousing, and the hides so produced shall not be eligible for certification unless the cooperative producing plant is an approved cooperative plant at the date of certification.

In respect to South American Hides, the same shall be eligible for certification only if produced at one of the plants named in the official list of approved plants on file with the Secretary of the Exchange. Such list shall be subject to the control of the Board Hide Trade Group, and names may be added to, or removed therefrom, and grades enumerated in Subdivision (9) of this section produced therein may be included or excluded from eligibility for certification upon the recommendation of the Committee on Grading and Warehousing, with the approval of not less than three (3) members of the Board Hide Trade Group. If a name shall be removed from said list, or if a grade produced in an approved plant shall be removed from eligibility for certification, the hides produced in such plant, or said grade, as the case may be, shall be eligible for certification for a period of three months thereafter, provided said hides otherwise conform to the specifications and requirements of the By-Laws, Rules and Regulations of the Exchange. Such additions or exclusions shall not be considered as affecting the amount of money to be paid or the grade or quality of hides to be delivered, or altering the monetary value of outstanding contracts. At any time the Committee on Grading and Warehousing, with the approval of the Board Hide Trade Group, may require that South American Hides shall be accompanied by such documents as to origin as may be deemed desirable.

(3) ORIGINAL RUN

All lots tendered for certification must be in their original run.

(4) CURE

Domestic Hides shall be delivered out of first salting only. They shall be cured with good rock salt, in properly built packs, in well regulated cellars (or floors) suitably

‡ Adopted April 2, 1934.

equipped and maintained; or cured by proven and accepted methods of brining or special cure. If cured only in salt pack, the minimum time of curing shall be thirty days from the closing date of the pack. Cows and steers may be salted together. Except in the case of "Pacific Coast" Hides, if branded hides are salted with native hides and are not separately marked when put into pack, the charge for inspection for certification shall be double the prevailing charge.

South American Hides shall be cured and delivered in accordance with the accepted

and approved standards prevailing at the point of origin.

(5) TAKE-OFF

Hides to be eligible for certification shall be well flayed by expert butchers or skinners, with cuts, scores, knife marks and other defects not in excess of the allowances provided in the By-Laws, Rules and Regulations.

(б) TRIM

Hides to be eligible for certification shall be trimmed as follows: Dewclaws, excess fat and meat, ears, snouts, lower lips, and any other portion of the animal which is removed in accordance with accepted standards shall be trimmed in the green state prior to salting. Hides shall further be substantially free from sinews, cut or split shanks or cut or split heads.

(7) TAKE-UP

Hides must be taken up from original packs of one producing plant and submitted for certification in lots within the limits of one contract unit. Each lot shall consist of one grade of hides, as defined in subdivision (9) hereof, except as otherwise specially provided in the By-Laws, Rules and Regulations. Each lot shall consist of the take off of not more than two successive seasonal periods, as provided in the By-Laws, Rules and Regulations. Hides shall be taken-up at the producing plant on such selected basis as is required in the By-Laws, Rules and Regulations. Domestic hides must be shipped direct from producing plant to Exchange licensed warehouse.

All necessary details in respect to selections, tare allowances and other factors shall be indicated on the producing plant's weight notes or by separate anthenticated statement of the producer. The methods to be used in determining grade, cure, test weights, allowances for moisture, condition, manure, grubs, warts, or other factors as specified or required in the By-Laws, Rules and Regulations, shall be in accordance with the accepted customs and standards prevailing at the time the hides are offered for certification.

(8) AGE LIMITATIONS

No Domestic Hides shall be eligible for certification which have been in original salt pack (when cured only in salt pack) for less than thirty days after the closing date of the pack; or which have been in pack for more than eighty days after the closing date of the pack; provided however, that the hides shall not have been in pack which has been in the making for more than sixty days. After hides have been taken out of pack, they shall be promptly placed in licensed warehouse; and transportation to licensed warehouse shall be direct and unbroken. Hides in licensed warehouse must be submitted for certification not later than 90 days after date of removal from salt pack.

No South American Hides shall be eligible for certification, which have been in original salt pack in plant of origin for less than twenty-one days after the closing date of the pack (under the present brining and curing method); or which have been in such salt pack for more than eighty days after the closing date of the pack; provided however, that the hides shall not have been in pack that has been in the making for more than thirty days. After hides have been landed in the United States they shall be promptly placed in licensed warehouse and transportation to licensed warehouse shall be direct and unbroken. Hides in licensed warehouse must be submitted for certification not later than 150 days after date of removal from original salt pack.

The Inspection Bureau shall determine the date of the opening of the pack, the date of the closing of the pack, and the date when the hides were removed from the pack.

Domestic Hides cured by proven and accepted methods of brining or special cure must conform strictly to such methods.

South American Hides shall be deemed cured by special cure.

(9) DELIVERABLE GRADES AND DESCRIPTION

Hides shall be graded and selected in accordance with the following table:

DOMESTIC

Grade	Description
Light Native Cows	Unbranded Cow Hides
	23 to 53 lbs. and may contain Ex-Light Native Steers—23 to 48 lbs.
Ex-light Native Steers	Unbranded Steer Hides
Sieers	23 to 48 lbs.
Native Steers	Unbranded Steer Hides
	Heavy—58 lbs. and up Light—48 lbs. to 58 lbs.
Butt Branded Steers	Steer Hides being branded on the butt area (back of break in flank)
	Heavy—58 lbs. and up Light—48 lbs. to 58 lbs.
Heavy Texas Steers	Steer hides branded on either side or butt and/or both sides and butts, but of compact, narrow, close pattern and plump.
	58 lbs. and up
Light Texas Steers	Description same as Heavy Texas Steers
nects	48 to 58 lbs.
Ex-Light Texas Steers	Description same as Heavy Steers.
Medis	23 to 48 lbs.
Colorado Steers	Steer hides branded on either side or butt and/or both sides and butts
	Heavy—58 lbs. and up Light—48 lbs. to 58 lbs.
Heavy Native Cows	Unbranded Cow Hides
COWS	53 lbs. and up
Branded Cows	Branded Cow Hides
	All weights (23 lbs. and up) and may include Branded EX-LIGHT STEERS, 23 to 48 lbs.
Native Cows and Steers	Unbranded Cow and Steer Hides
(All Weights)	All weights (23 lbs. and up)
Applicable on ly to hides delivered against the "Old Standard Contract"	The standard of take-off for this grade may include a greater proportion of cut hides than the standard for the above-mentioned grades, but a standard lot shall not contain more than 5% cut hides and/or a greater proportion of scores, knife marks, or other defects than is customary in a take-off containing said maximum percentage of cut hides.

DOMESTIC-Continued

GRADE

DESCRIPTION

Branded Cows and Steers (All Weights) Branded Cow and Steer hides
All weights (23 lbs. and up)

re: "Old Stand- {
ard Contract" }

Same standard of take-off as prescribed for Native Cows and Steers (All Weights) grade,

"Pacific Coast" Native and Branded Cows

Unbranded and Branded Cow hides

Produced in plants known in the trade as West Coast plants.

All weights (23 lbs. and up)

rc: "Old Stand- { ard Contract" }

Same standard of take-off as prescribed for Native Cows and Steers (All Weights) grade.

"Pacific Coast" Native and Branded Steers Unbranded and Branded Steer hides

Produced in plants known in the trade as West Coast plants.

All weights (23 lbs, and up)

re: "Old Stand- \
ard Contract" \

Same standard of take off as prescribed for Native Cows and Steers (All Weights) grade,

Weights specified in this table are net after deduction of tare

SOUTH AMERICAN

()	RΛ	DE	

Description

"Frigorifico" Extreme Light Cows and Steers

Usual Frigorifico Standard

Shipping range 8 to 18 kos., with maximum shipping range of 16 kos.

No selection for weights shall be made within the range of the pack as salted.

"Frigoritico" Cows Usual Frigorifico Standard

Shipping range 18 kos, and up

"Frigorifico" Heavy Steers Usual Frigorifico Standard

Shipping range 22 kos, and up

"Frigorifico" Light Steers

Usual Frigorifico Standard

Shipping range 17 to 23 kos.

(10) SELECTION AND SELECTION FACTORS FOR DOMESTIC HIDES

(a) Selection and Selection Factors for Domestic Hides shall be as follows:

No. 1 Selection comprises hides which are:—

Sound and fully cured

Standard pattern

Free from cuts or holes through the hide

Free from slips

Free from warts; except as otherwise provided in subdivision (d) hereof

Free from sores, scabs or rubs, damaging to grain

Free from a deep score in the body of the hide Having less than 5 grubs, either open or which can be skewered

No. 2 Selection comprises hides which are:

Free from warts; except as otherwise provided in subdivision (d) hereof

Hides which will not grade into the No. 1 Selection, but which qualify within the limits of a No. 2 Selection, as generally accepted in the trade

(c) Hides which are inferior to No. 2 Selection and/or hides affected by the following characteristics are not tenderable for certification, and must be removed before a lot is offered for certification.

a. Hides damaged by warts in excess of such as will grade into No. 2 Branded selection.

b. Hides affected by contagious disease.

c. Glue or fallen hides.

d. Worm-eaten hides.

e. Hides damaged by other causes.

f. Lots salted down with an excessive amount of previously used salt shall not be eligible for certification.

The following grades shall be subject to the above selection specifications with the modifications set forth below:-

Colorado Steers

Selection may include Native Steers having warty damage not exceeding a portion in size of an ordinary brand.

Selection may include any Branded Steers having warty damage not exceeding in size that of an ordinary brand, or Native Steers having warty damage not exceeding in size that of two ordinary brands.

Branded Cows.

Selection may include Native Cows damaged by warts in a No. 1

portion not larger than that of an ordinary brand. Selection may include Native Cows damaged by warts, in a portion no greater than that of two ordinary brands, or a Branded Cow having warty damage no greater than that of one ordinary brand.

Branded Cows and Steers (All Weights)

Same exception as set forth herein for Branded Cows and Colorado Steers respectively.

"Pacific Coast" Native and Branded Cows

Same exceptions as set forth herein for Branded Cows.

"Pacific Coast" Native and Branded Steers

Same exceptions as set forth herein for Colorado Steers.

Basis Grade

Sec. 826.* Contracts entered into on the Exchange shall be deemed to be for Standard No. 1 Light Native Cows—July, August or September take-off. The seller shall have the option of delivering any one of the tenderable grades specified in Section 825 subdivision (9) of these By-Laws, at the differentials fixed in the By-Laws with adjustment for other seasonal periods of take-off, as provided in Section 828 and Section 829 of these By-Laws, and with adjustment for quality, tare, selection, special factors, weight and trim, as provided in the By-Laws, Rules and Regulations.

^{*} Adopted April 2, 1934.

Contract Unit

Sec. 827.† In the fulfillment of every contract, the seller must deliver a certificated lot of 40,000 lbs. (5 percent more or less) of hides of one grade, except as otherwise specifically provided in the By-Laws, Rules and Regulations.

Differentials

SEC. 828.‡ For Domestic Hides, the differentials set forth in the following table are fixed between the Standard basis grade and the Standard respective grades—July, August or September take-off. For South American Hides the differentials are fixed between the Standard basis grade and the Standard respective South American grades—December, January or February take-off.

Premium Grades

"Frigorifico" Heavy Steers	premium	1‡ cents per	pound
"Frigorifico" Extreme			
Light Cows & Steers		d cent per	
"Frigorifico" Cows		dent per	
"Frigorifico" Light Steers	— premium	½ cent per	pound

Grades Deliverable at the Basis Price

Light Native Cows	— Basis
Ex. Light Native Steers	- No premium or discount
Heavy Native Steers	- No premium or discount
Heavy Butt Branded Steers	No premium or discount
Heavy Texas Steers	No premium or discount

Discount Grades

- discount	1 cent per pound
discount	deent per pound
discount	dent per pound
discount	dent per pound
- discount	dent per pound
	•
discount	1 cent per pound
discount	1 cent per pound
discount	11 cents per-pound
discount	14 cents per-pound
	— discount

Adjustment for Seasonal Period of Take-off

SEC. 829.*

(1) In respect to Domestic Hides the take-off of seasonal periods other than July, August or September take-off, shall be adjusted by deducting from the net weight of the lot tendered for certification after adjustment for tare and trim, if any, a percentage thereof upon the basis set forth in the following table:

Period of Take-off	Percentage Weig Deduction
July—August—September	None
October	10%
November	3%
December	5%
January February—March	7%
April	1044 754
May	4%
June	20%

[†] Adopted April 2, 1934. ‡ Adopted April 2, 1934.

^{*} Adopted April 2, 1934.

(2) In respect to South American Hides, the take-off of seasonal periods other than December, January or February take-off, shall be adjusted by deducting from the net weight of the lot tendered for certification, after adjustment for shrinkage and tare, if any, a percentage thereof upon the basis set forth in the following table:

Period of Take-off	Percentage Weight Deduction
December—January—February	None
March	2%
April	4%
May	5%
June—July—August	7%
September—October	5%
November	3%

(3) Each group of successive months carrying a separate percentage of adjustment shall be considered a single seasonal take-off period for the purposes of these By-Laws and Rules.

Discount for Special Factors

SEC. 830.*

(1) On deliveries of Domestic Hides the seller shall make an allowance to the buyer of 1c per pound for all hides of No. 2 selection (including grubby hides) contained

in the lot, within the limits of an original run, as provided in these By-Laws.

(2) On deliveries of Domestic Hides, an allowance of ½c per pound shall be made by the seller to the buyer on all cut throat hides contained in the lot, provided however, that in respect to hides originating in plants which are approved by the Grading and Warehousing Committee and where it is customary to deliver cut throat hides, the allowance of ½c per pound for cut throat hides in the lot shall not be imposed, and the Inspection Bureau shall indicate on the Hide Certificate that the lot carries no allowance for cut throats.

(3)† When the hides deliverable against the "New Standard Hide Contract" have been out of original salt pack for more than twelve months,—the seller shall make a cumulative compensation allowance to the buyer of two one-hundredths (2/100c) of one cent per pound per month, computed on the adjusted net weight, commencing with the thirteenth month after the calendar month of removal of the hides from original salt pack and up to and including the month in which delivery on Exchange contract is completed.

(4)‡ In the event that South American Hides by accepted custom are delivered with an allowance for cut throat hides contained in the lot, such an allowance shall be

granted on deliveries of such hides on Exchange Contract.

(5) On deliveries of Domestic Steer Hides, excepting "Pacific Coast" grades and "all weight" grades, where heavy and light hides are deliverable together, an allowance of 1c per pound shall be made by the seller to the buyer for all light hides contained in the lot, within the limits of an original run, as provided in these By-Laws.

Special Factors Relating to Deliveries and Invoicing of Hides

SEC. 831.**

(1) Each contract unit shall be invoiced and delivered on a final adjusted net

weight of not more than 42,000 pounds nor less than 38,000 pounds.

(2) When a contract unit consists of hides taken-off during any two successive seasonal periods, the weight adjustment shall be fixed on the basis of the greater deduction of the two seasonal periods.

(3) When a contract unit of Colorado Steers includes Butt Branded Steers, the same shall be invoiced as Colorado Steers, with no adjustment for the Butt Branded

Steers contained in the lot.

(4) On all deliveries of South American Hides there shall be added to the weight as determined by the Inspection Bureau before deduction for seasonal period of take-off, 5 percent of the actual weight as an offset for shrinkage in transit.

^{*} Adopted April 2, 1934.

[†] Adopted Aug. 1, 1938.

[#] Adopted April 2, 1934.

^{**} Adopted April 2, 1934.

(5) On all deliveries of Domestic Hides, where the trim is superior to that specified in these By-Laws, there shall be added to the weights before deduction for seasonal period of take-off by the Inspection Bureau, such a percentage thereof as shall be fixed by the Committee on Grading and Warehousing, with the approval of not less than three (3) members of the Board Hide Trade Group, as a credit for such superior trim, provided that such superior trim, and a weight adjustment therefore, is in accordance with the then accepted customs and standards.

Changes in Standards Affecting Grades and Selections of Hides

SEC. 832[†] Hides shall conform in respect to grading, selection, selection factors, shipping range, and other provisions of these By-Laws relating to the grade and classification thereof, to the accepted standards, from time to time, for each respective grade. Until change is made in such standards, as hereinafter provided, the standard grades, selections, selection factors and shipping ranges shall be deemed to be as prescribed in

Section 825 of these By-Laws.

If and when changes shall be made in such accepted standards, the Board Hide Trade Group, subject to the approval of not less than three (3) members of said Board, may, upon recommendation of the Committee on Grading and Warehousing, approve a revision of the grading provided in the By-Laws, based upon such changed standard. The Grading and Warehousing Committee shall thereupon fix differentials for the revised grades, or change the differentials provided herein, if such change is deemed necessary. The grades as theretofore adopted shall continue to be deliverable through the current month and the next succeeding twelve (12) months after such change becomes effective; and the differentials fixed herein for said grades shall continue to prevail during said period.

Such changes shall not be deemed to affect the grade or quality of hides to be deliv-

ered on outstanding contracts or the amount of money to be paid thereon.

Hide Rules

Hours for Trading in Hides

Rule, 1.* The hours for trading shall be from 10:10 A. M. to 3 P. M. except on Saturdays when trading shall cease at 12 o'clock noon.

Call for Hides

RULE. 2† A call for the purchase and sale of hides for future delivery shall be held in the Exchange Room on each business day, at the hour prescribed for the opening of trading in hides as provided in Hide Rule 1, and shall be conducted by a person design

nated by the President.

The call shall be by months, beginning with the current month, except when trading in the current month has ceased, in which event it shall begin with the next succeeding month and the call shall continue until twelve subsequent calendar months have been called, after which the call shall stand adjourned. In respect to the "New Standard Contract," the call shall begin with the month of September, 1938.

Delivery Months for Trading in Hides

Rule 3.1 (a). (Deleted 4/1/35.)

(b) No contracts for the delivery of hides shall be made or recorded for any month except the current month, or one of the twelve succeeding months, provided that with respect to the "New Standard Contract" no contracts for the delivery of hides shall be made or recorded for any month earlier than the month of September, 1938. Trading in the month following the twelfth succeeding month may commence on the opening call following the last business day upon which transferable notices may be issued for delivery in the current month.

Price Multiples for Hides

Rule 4. Prices for hides on future delivery contracts shall be in multiples of one-hundredth of one cent per pound. Contracts made on any other basis are prohibited.

- † Adopted April 2, 1934.
- * Amended May 7, 1934.
- ** Amended April 2, 1934, Aug. 1, 1938.
- ‡ Amended April 2, 1934, April 1, 1935, Aug. 1, 1938,

Price Fluctuation Limitation for Hides

RULE. 5.* Trades for future delivery of Hides in any month shall not be made, during any one day, at prices varying more than two cents per pound above or below the lowest price of the closing range of such month as established by the Committee on Quotations at the close of the preceding business session of the Exchange.

The foregoing limitations shall not apply to trading in the delivery month during the period in which Transferable Notices for delivery therein may be issued unless

otherwise determined by the Board.

At the discretion of the Board, any limit of trading herein provided for may from time to time and without previous notice be changed or suspended or temporarily modified.

The affirmative vote of a majority of those present, but in no event less than twelve members of the Board, is necessary to effect any change in the foregoing provisions.

Placing Hides in Deliverable Condition

RULE 6. Hides tendered against Exchange contract must at the seller's expense be bundled and tied, and if required by the Committee on Grading and Warehousing, with the approval of the Board Hide Trade Group, shall be tagged in such manner as shall be prescribed.

Delivery and Payment for Hides

Rule 7.** (a) Only certificated hides shall be tenderable against the hide contract.

Said hides shall be delivered only from licensed warehouses.

(b) Negotiable warehouse receipt as provided for in these By-Laws, signed by the warehouseman, indorsed by the member in whose favor it is drawn, and accompanied by a hide certificate or validated notice of grade (also certifying to the adjusted net weight), issued by the Inspection Bureau, shall be a good delivery in fulfillment of a contract on which such delivery is made and the member receiving the same shall return the Transferable Notice to the member making the delivery. The delivery of hides shall be considered complete when warehouse receipt and a hide certificate or validated notice of grade, as above provided, shall have been delivered to the receiver. All hides must be delivered with "labor in" and storage charges paid to and including the second business day following the day of delivery.

In the event that storage must be paid upon any other than a per diem basis, the receiver shall not be obligated to refund to the deliverer any storage prepaid beyond the second business day following the day of delivery. The weight as noted by the Inspection Bureau on the hide certificate shall be binding upon all parties.

(c) Written notice of the holding of the Transferable Notice shall be given by the last acceptor thereof, before four o'clock P.M. on the day on which such Transferable Notice was issued, or on the last notice day before nine o'clock A.M. on the next business day, to the member issuing the Transferable Notice which notice shall be accepted as a legal demand for the hides. The issuer of the notice shall, before two o'clock P.M. on the day of delivery, tender to the member holding said Transferable Notice, a warehouse receipt in the manner and form hereinbefore provided, together with a hide certilicate or validated notice of grade issued as provided in paragraph (b) of this Section for about 40,000 pounds of hides to be in one warehouse.

(d) An invoice for the hides, giving the marks and numbers of the hides and the name and number or letter of the warehouse, shall be rendered before eleven o'clock A.M. on the day of delivery with adjustment for premium or discount, if any, for grade, and discounts for special factors and such other allowances and credits as are provided for in these By-Laws and Rules. Provided, however, that when the delivery of warehouse receipt becomes due upon the last day of any month, bills shall be rendered at or before one o'clock P.M. on that day and payment shall be made as hereinbefore provided

at two-thirty o'clock P.M. on the same day.

(e) The member receiving the warehouse receipt, accompanied by a hide certificate issued by the Inspection Bureau (or validated notice of grade) covering the entire contract delivered, shall at once make payment to the member presenting the same by a certified check.

(f) Where a validated notice is tendered on a delivery instead of a hide certificate, the payment shall be made on the basis of 35,000 pounds of the grade tendered less the

* Amended Sept. 25, 1939.

^{**} Amended April 2, 1934, April 1, 1935, Aug. 1, 1938.

[†] Amended April 1, 1935.

maximum discount from standard and less the largest seasonal period discount for the particular grade of hides delivered, pending issuance of the hide certificate.

(g) The receiver shall pay the deliverer one-half of the charges for the original certification of hides.

Hides Damaged by Fire, Smoke, Water or Other Causes

Rule 8. Any hides damaged by fire, smoke, water or by other causes, shall not be

good delivery on contract.

In the event of fire, flood or other contingencies which may cause damage occurring in a licensed warehouse in which certificated hides are stored, the Inspection Bureau shall cause one of its inspectors to inspect the hides stored in said warehouse, and said inspector shall make a report showing by lot number the hides which have been damaged by fire, smoke, water or other causes, and are not in good, sound and merchantable condition, and such list shall be at once posted upon the bulletin board of the Exchange and no lot of hides on the list shall thereafter be a good delivery on contract.

Title to Hides

RULE 9. Title to hides shall vest in the buyer upon exchange of certified check for delivery documents. In all cases, the hides shall be at the risk of the seller until title vests in the buyer.

Transferable Notice for Hides

Rule 10.* Every notice of delivery issued by the seller pursuant to a "Old Standard Hide Contract" shall be for 40,000 pounds (5% more or less) and shall be in form as follows:

(The blank spaces provided for various information on the Transferable Notice form must be filled in by the issuer.)

COMMODITY EXCHANGE, INC. Transferable Notice OLD STANDARD HIDE CONTRACT

İ	New York	19
Take notice that on	bout 40,000 pounds of ${ m W}$	et Salted Hides
in good, sound, merchantable condition of the		
with the following discount from Standard:		
taken off during the month or months of		
at packer plant known as		
located		
removed from original salt pack		
at the Transferable Notice price of		ents per pound.
Said hides will be delivered CERTIFIC.	$\Lambda { m TED}$ (Certificate $rac{Old}{New}$	form Expires
) from licensed warehou (Date)	•	
located atknown as		

We pledge ourselves to deliver on the day specified for delivery, to the last holder hereof, documents as provided for in RULE 7 upon written notice of the holding of this notice given to us by the last holder hereof before four o'clock P.M. on the day this notice is issued, (except that the transferee who becomes the last acceptor of this notice after four o'clock P.M. on the last notice day for delivery in the current month must notify us before nine o'clock A.M. on the next business day).

^{*} Amended April 2, 1934, April 1, 1935, May 25, 1936, Aug. 1, 1938, Aug. 22, 1938.

This notice is to be delivered to us simultaneously with our delivery of the abovementioned delivery documents to the holder hereof and our receipt of check in payment for said hides.

Signed (L. Bros.)

Conditions

Each of the acceptors agrees that the last acceptor hereof will before four o'clock P.M. on the day this notice is issued, or as otherwise required give written notice of the holding of this notice to the issuer hereof and on the delivery day specified herein receive from the issuer a warehouse receipt together with a certificate of grade or a validated notice of grade, as provided in the By-Laws, for about 40,000 pounds of hides, and pay the issuer hereof at the transferable notice price hereinbefore specified, settling with them on the basis of Standard No. 1 Light Native Cows,—July, August, September,—take-off, with additions or deductions for variation in grade, in accordance with the differentials established by the By-Laws, with other debits and credits as provided for in the By-Laws and Rules of the Exchange. It is further agreed that each acceptor hereof shall continue his (or their) liability to each other for the fulfillment of the contract until this notice shall have been returned to the issuer and the delivery documents required by the By-Laws and Rules shall have been received by the last acceptor hereof, at which time all responsibilities of intermediate parties shall cease.

Signed (H. Bros. & Co.)

Form of Transfer

New York......19....

Time Received

Accepted by

Transferred to

(11:37 A. M.)

(H. Bros. & Co.) (G. & Co.)

Every notice of delivery issued by the seller pursuant to a "New Standard Hide Contract" shall be for 40,000 pounds (5% more or less) and shall be in form as follows:

(The blank spaces provided for various information on the Transferable Notice form must be filled in by the issuer)

COMMODITY EXCHANGE, INC. Transferable Notice

NEW STANDARD HIDE CONTRACT .

Adopted Aug. 1, 1938

New York	
Take notice that on	in accordance with the terms at 40,000 pounds of Wet Salted
Hides in good, sound, merchantable condition of the fo	ollowing grade,
Standard:	
taken off during the month or months of	
at packer plant known aslocated	
removed from original salt pack	
compensation allowance of 2/100c per pound per month c	ommences
(Date)	
at the Transferable Notice price of	Certificate Expires
) from licensed warehouse in the City of	
known as	located at

We pledge ourselves to deliver on the day specified for delivery, to the last holder hereof, documents as provided for in RULE 7 upon written notice of the holding of this notice given to us by the last holder hereof before four o'clock P.M. on the day this notice is issued, (except that the transferee who becomes the last acceptor of this notice after four o'clock P.M. on the last notice day for delivery in the current month must notify us before nine o'clock A.M. on the next business day).

This notice is to be delivered to us simultaneously with our delivery of the abovementioned delivery documents to the holder hereof and our receipt of check in payment

for said hides.

Signed (L. Bros.)

Conditions

Each of the acceptors agrees that the last acceptor hereof will before four o'clock P.M. on the day this notice is issued, or as otherwise required give written notice of the holding of this notice to the issuer hereof and on the delivery day specified herein receive from the issuer a warehouse receipt together with a certificate of grade or a validated notice of grade, as provided in the By-Laws, for about 40,000 pounds of hides, and pay the issuer hereof at the transferable notice price hereinbefore specified, settling with them on the basis of Standard No. 1 Light Native Cows, -July, August, September,—take-off, with additions or deductions for variation in grade, in accordance with the differentials established by the By-Laws, with other debits and credits as provided for in the By-Laws and Rules of the Exchange. It is further agreed that each acceptor hereof shall continue his (or their) liability to each other for the fulfillment of the contract until this notice shall have been returned to the issuer and the delivery documents required by the By-Laws and Rules shall have been received by the last acceptor hereof, at which time all responsibilities of intermediate parties shall cease.

Signed (H. Bros. & Co.)

(a)* Every notice of delivery for Hides issued by the seller pursuant to a contract for future delivery shall be issued to the buyer before 9 A.M. on the fourth business day (Saturdays excepted) prior to the day of delivery, except on the last notice day for delivery in the current month, when such notices may be issued not later than 12:30 P.M. With respect to the "Old Standard Hide Contract" the last delivery day in the month shall be the second full business day immediately preceding the last business day in the month.

All Transferable Notices issued to the Clearing Association clearing Hide Contracts shall be delivered to the Clearing Association, in accordance with such regulations as the Clearing Association may adopt.

- (b) † All Transferable Notices shall be officially numbered by the Clearing Association before circulation. Issuers of Transferable Notices when presenting same to the Clearing Association for numbering shall submit therewith a signed memorandum addressed to the Exchange, stating the amount and description thereof, and after certification by the Clearing Association this memorandum shall be delivered to the Exchange for the purpose of recording the details with respect to the Transferable Notices issued.
- (c) The party receiving a notice may transfer it to another party, and it may be given by one transferee to another. Every party receiving the notice shall indorse upon it the time of receipt. The member first receiving a notice issued before the opening of trading in hides shall have forty-five minutes after the said opening in which to transfer it; but in every other case except where a notice has been lodged with the Clearing Association, a notice must be transferred within thirty minutes after the time of receipt. Any party, except the Clearing Association, who fails to forward such notice within that time shall be liable to a penalty of fifty dollars per contract, payable to the Exchange, or to have the notice returned to him, at the option of the party with whom the notice lodges at the close of the day.

^{*} Amended May 25, 1936, Aug. 22, 1938, † Amended May 25, 1936.

(d) All transfers must be made within the hours for trading in hides except transfers of a notice issued for delivery on the last delivery day of the month, which may be made till the interest in such month is liquidated but not later than midnight of the day of issue.

(e) The Clearing Association shall return to the last acceptor thereof any notice which has not been forwarded at the close of the Exchange on the day of issue, or by

midnight on the last notice day of the month.

(f) Any member receiving a notice forwarded by the Clearing Association, during the hours it is permissible for such notice to circulate, must accept the same regardless of the period of time such notice may have been held by the Clearing Association.

(g) Should the office of a party to whom a notice is to be given be closed, it shall be good service to give the notice to the Secretary of the Exchange who shall indorse thereon the day and time of its receipt and post notice thereof on the bulletin board of the Exchange.

(h) Every notice, issued and tendered as herein provided, shall be accepted by any member of the Exchange on any contract for the future delivery of hides for the delivery

month therein named.

(i) The difference between the price of every contract on which such notice is tendered and the price at which the notice is issued shall be paid on the day following the date of the notice.

(j) The failure on the part of the holder of any notice to notify the issuer thereof, as provided therein, shall subject him to a penalty of fifty dollars for each notice, to be

paid to the issuer thereof, the contract to remain in full force.

(k) The Secretary shall, at the close of the Exchange on the day previous to each notice day, post upon the bulletin board of the Exchange the price at which transferable notices shall be issued on the following day. The transferable notice price shall be the approximate closing price of the current month on the day previous to notice day.

(1) Hides shall be paid for at the transferable notice price. The difference between

(1) Hides shall be paid for at the transferable notice price. The difference between said price and the settlement price of the day previous to delivery, as determined by the Clearing Association shall be adjusted separately on the basis of 40,000 pounds basis grade, without adjustment for seasonal period of take-off or other additions or deductions

provided for in the By-Laws and Rules.

(m) No member of the Exchange shall make a fictitious use of any name to fill up the time in the issue or transfer of any notice for the future delivery of hides. Any member who shall be found guilty thereof by an arbitration, or, if an appeal be taken by the Board of Appeals, shall, in each case, pay to the party with whom the notice may lodge at the close of the day a penalty of one hundred dollars, and in addition thereto may, upon a repetition of the offense, be suspended by the Board of Governors.

(n) All Saturdays and such holidays as are prescribed by the By-Laws or ordered by the Exchange or by the Board as a whole, shall be observed as holidays so far as concerns the issuing of transferable notices or the delivery of delivery documents in ful-

fillment of contracts for future delivery, except as hereinafter provided.

(a) When the last day on which a transferable notice may be issued for delivery in the current month is declared a holiday too late for the issuance thereof on the preceding notice day, such notice may be given or transferred in the usual manner on such holiday.

(p) When the last delivery day of the current month is declared a holiday too late for a transferable notice to be issued requiring delivery on the preceding business day,

then the delivery shall be completed on said holiday.

(q) Members having contracts open in the current month must keep their offices open for the purpose of receiving such notices or of completing such deliveries.

Return Commission for Obtaining Business Unguaranteed and Guaranteed Accounts

Rule, 11. Pursuant to Commission Law Rule 628 the return commission on a contract for future delivery of hides bought or sold shall be:

(a) On unguaranteed accounts, not more than Four Dollars on each contract.

(b) On guaranteed accounts, one-half of the domestic non-member rate of commission on each contract, but there shall be deducted from the procuring member's share of such commission an amount equal to the rate of floor brokerage on said transaction, whether paid or not.

Fees paid on such transactions pursuant to Sec. 209 of the By-Laws shall be deducted

from any return commissions paid to a member.

The Tanner and the Hide Exchange

To the extent that a tanner cannot sell leather for future delivery before he has purchased the hides with which to make the leather, he must gamble on the fluctuations of the hide market during the interim between purchase of hides and sale of leather unless he can sell the gamble to someone else, and this the Hide Exchange provides him with facilities for doing. Retention of this gamble has been disastrous to some tanners, and many tanners cannot afford to gamble. There are many speculators who desire to gamble on the hide market and the Hide Exchange provides the market place for the tanner to sell a gamble that he does not want to a speculator who does want it in the hope of making a profit.

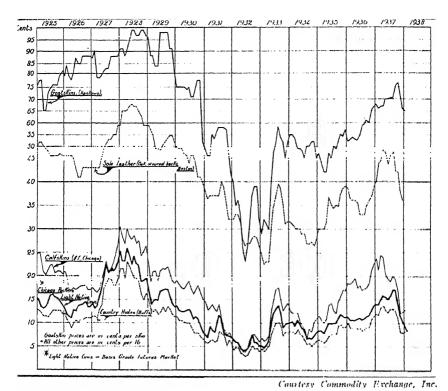


Fig. 85. Market Price Fluctuations in Goatskins, Calfskins, Country Cow Hides, Sole Leather and Packer Light Native Cow Hides from 1925 to 1938.

The gamble lies only in the virtual ovenership of the hides and not in mere physical possession. The tanner requires physical possession of hides in order to make leather, but he may not desire the gamble that goes with virtual ovenership. The pure speculator desires the gamble, but not physical possession and so he must acquire virtual ovenership without physical possession. By providing facilities for buying and selling hide futures contracts, the Exchange furnishes the tanner with a sound method for separating virtual ovenership from physical possession and selling only the virtual ovenership to the speculator.

The tanner can sell the gamble not only on his raw stock, but also on his actual leather simply by selling hide futures contracts to cover the raw-stock value of his possessions. What he sells need not be of the same character as the stock he possesses provided its market variations parallel those of the stock he has on hand. For example, a goatskin tanner would hedge against his stocks of both raw skins and leather by selling light native cow hides in the form of futures contracts. Fig. 85 shows the parallel fluctuations in market prices of goatskins, calfskins, country hides and sole leather with those of packer light native cow hides over the period 1925 to 1938. Although the ratios are not constant, the major trends of the values are nearly enough parallel to permit a goatskin tanner to eliminate some of his gamble by selling cow hides.

Effect of Speculation on the Hide Market

Many tanners have condemned the Hide Exchange on the ground that it is a lure to gamblers, whose speculations increase the violence of the fluctuations of hide prices. Actually, it has had two effects, one running contrary to the other; since the hide-futures market came into existence in 1929, the extreme ranges of prices from high to low over a year have actually been *smaller* than before, and in that sense the Hide Exchange has been responsible for stabilizing the market. On the other hand, the month-to-month fluctuations have been *greater* than before. Whether this is an advantage or a disadvantage to a tanner must depend in a large measure upon the flexibility of his purchasing of hides, the intimacy of his knowledge of the causes of price fluctuations and the extent to which he uses the facilities of the Hide Exchange for his own safety. For most tanners to make profits, it appears to be necessary to master the complications involved in buying and selling both raw hides and finished leather to at least the same extent as he must master the complications involved in manufacturing leather efficiently.

The natural rise and fall of hide prices is caused by a fluctuating supply and demand. If prices fall to unnaturally low levels, certain banking houses are always ready to invest their money in them with reasonable assurance of earning at least the interest on their money by holding them until a more rational basis is established in the hide market. When prices rise to unnaturally high levels, all holders of hides feel the urge to sell, whether to get rid of their holdings at high prices or merely to hedge to protect the paper gains they have made. The effect of the speculator is to add buying power to the market when it is low and to add selling power to the market when it is high. This has the effect of keeping the market from going as low as it might otherwise go and preventing it from going as high as it might otherwise go. On the other hand, the additional buying and selling power of the speculator increases the violence of the market fluctuations over short periods.

Avoiding The Gamble of Hide-price Fluctuations While Making an Assured Profit on the Sale of Hide Futures

Under the foregoing title, the writer published an article in the *Shoe & Leather Reporter* which has received some favorable comment and which is reproduced in the following paragraphs. Although it involves some repetition, it emphasizes a number of important points.

"The manufacture of leather involves a gamble that is unique among large industries. The primary reason for this is that the *production* of leather bears no relation to the demand for leather, except over relatively short periods of time. Hides and skins are a by-product of the meat-packing industry and practically

every hide or skin made available is eventually tanned into leather. An increased demand for leather does not result in increased slaughter and availability of hides, but merely in an increase in the price of both hides and leather. It is thus inevitable that hide prices must fluctuate rather widely.

"The leather industry today has become one of the most highly competitive of all major industries. So keen has become this competition that the tanner is fortunate indeed who can be assured of a net profit of one-half cent per pound on the raw stock that he tans. But this hoped-for profit represents only a small fraction of the variation in market prices for hides. Fig. 83 shows the variations in market prices of light native cow hides for the past thirty years. They range from a low of 4½c to a high of 61c per pound. The figures were furnished by Mr. James Price, Jr. of Pratt Bros. Co., New York and Chicago, publishers of Pratt's Reports and the Daily Hide and Leather Market. Monthly prices are taken as of the first of the month and these are averaged to get the yearly values shown in the chart. The high and low values for each year are taken as the high and low monthly values for that year and not as the extreme high and low values for single sales. The values for 1940 are for the first nine months.

"During the first nine months of 1940, the market price of light native cows has fluctuated over the range 10½c to 15c and that of butt-branded steers over the range 9¼c to 14½c. Since it may take from a month to a year to sell the leather after buying the hides, it is evident that the tanner is of necessity a gambler in a big way.

"Sound business cannot well be based on speculation. With the hide cost usually representing more than one-half of the selling price of the leather and with hoped-for profits representing only a fraction of hide-price fluctuations during the time the tanner has the stock in his possession, it would seem essential to survival for a tanner to take every precaution within his power to reduce the element of speculation to a minimum.

"A tanner requires physical possession of hides or skins in order to make leather for sale. But the gamble does not lie in the mere physical possession of hides, but rather in the virtual ownership. A man does not need to own a house to have a home; he can obtain possession of a house by renting it, leaving the ownership with his landlord. In this way, he escapes the danger of a crash in real estate prices. When a tanner buys a car of hides, he acquires both physical possession of those hides, which he must have to continue in business, and virtual ownership, which carries with it all of the gamble of a fluctuating hide market. The pure speculator in hide futures has no interest in the physical possession of hides, but he requires virtual ownership to provide him with the desired speculation. Commodity exchanges exist for the purpose of allowing holders of commodities to sell virtual ownership of those commodities, while retaining the necessary physical possession.

"In selling virtual ownership, it is not at all necessary for the tanner to sell ownership of the particular stock that he has in his possession; he accomplishes the same result by selling for future delivery anything whose market price fluctuates up or down in proportion to the market fluctuations of the stock in his possession. This operation is known as hedging; that is, making a bet to offset a bet already made. When a tanner buys raw stock, he may be considered to have bet that the market value of this stock will rise, or at least not fall. By selling hides for future delivery in amounts equivalent to that which he has purchased, he offsets his bet made in purchasing and neither gains nor loses in any subsequent market fluctuations; if the market subsequently rises, he gains in the increased value of

his inventory what he loses in covering on his sale of hide futures; if the market falls, he profits when covering on his sale of hide futures by an amount representing the shrinkage in the value of his inventory.

"No argument need be made here of the value of hedging as a price protection because it has been proved over the course of many years in all of the major commodity markets. If the market price of wheat moved up or down exactly in proportion to the market price of the hides represented in a tanner's inventory, he could hedge by selling wheat futures, but wheat prices and hide prices do not move together and so he must do his selling in futures in that commodity whose price fluctuates most nearly in direct proportion to the value of his inventory. For the tanner, that commodity is hides. Commodity Exchange, Inc., New York, provides an exchange dealing in hide futures. On this exchange, the basis grade on which trading is done is No. 1 light native cows of July, August or September take-off, but the seller of a hide-futures contract has the option of delivering any one of a number of grades, taking into account the specified premiums and discounts according to his choice of grade to be delivered. Since the market prices of all grades of hides and skins do not rise and fall in exact proportion, a tanner cannot hope to accomplish perfect hedging by selling hide futures, but by so doing he will come closer to eliminating the gamble of fluctuating hide prices than by any other method known to the writer.

"Let us assume that a tanner has decided to minimize, as far as possible, the gamble of a fluctuating hide market and consider just what he must do to accomplish this result. He must first calculate the raw-hide value of his inventory; that is, today's market value of the raw stock that is contained in his inventory, whether in the form of raw stock, leather in process or finished leather. He must then sell hide-futures contracts to the approximate value of this raw-stock inventory. He sells these contracts without any intention of making delivery, but solely as a hedge against a possible decline in the value of his inventory.

Avoiding the Gamble

"Let us assume that on November 1, 1940 the tanner had an inventory of which the raw-stock content was worth approximately \$100,000 on the hide market. A unit hide-futures contract calls for 40,000 lbs. of hides. If the June, 1941 futures market was 10c, he would have his broker sell for him 25 futures contracts deliverable in June, 1941. Virtual ownership of the raw-stock value of his inventory would now rest with the purchasers of his contracts and any future gamble of fluctuating hide prices would no longer rest with the tanner, but with the purchasers of the contracts. Since the tanner has no intention of making delivery on the contracts sold, he ultimately clears them before maturity by buying an offsetting number of contracts, usually within the month before maturity so as to avoid having to buy contracts under pressure. Meanwhile, if he increases his inventory by buying more hides in the spot market, he simultaneously sells additional contracts to keep his hide inventory sold at all times. If he decreases his inventory by selling leather, he simultaneously buys contracts to reduce his contracts sold to the lowered value of his inventory.

"Each time he clears contracts before maturity by buying equivalent contracts solely to avoid making delivery, he simultaneously sells new contracts in order to keep his inventory hedged at all times. This is a continuous process by which the tanner at all times keeps *virtual ownership* of the hide portion of the raw stock and leather in his possession in the hands of others desirous of speculating and he himself avoids the gamble of the fluctuating hide market.

"Many tanners have condemned the hide exchange as inviting speculators to play with a market already too speculative for the safe operation of the tanning industry. Actually, the effect of the speculators has been to lessen the extreme spread of hide prices over extended periods of time, while making them fluctuate more violently over shorter intervals. Whatever may be said for or against this effect, the fact remains that the speculator is a customer for the tanner who is trying to get rid of the element of gambling that exists in his hide purchases. If any

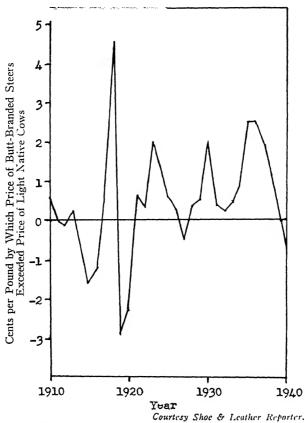


Fig. 86. Relative Price Variation of Butt Branded Steer Hides and Light Native Cow Hides by Years from 1910 to 1940.

tanner will review his hide purchases over a long period of time, the chances are good that he will find that he would have been money ahead had he followed the given procedure rigidly.

"Over the years, the tanner has of necessity become a natural speculator in hides and it is not easy for him to discard a lifelong habit. In order to hedge his inventory completely, he must give up those profits that accrued to him with every past rise in the hide market, but in exchange for this he escapes the losses that he suffered in declining markets. Some tanners find it distasteful to give up the old gamble of the hide market, but try to confine their speculations within limits

that they feel that they can afford. Some do this by only partially hedging their inventories and others by spreading their purchases so that the average cost remains close to the average market value, but complete safety really lies in complete hedging.

"As long as there are tanners who will sell leather below replacement costs and as long as relative market values of different grades of hides vary, a tanner cannot hope to achieve perfect hedging. A goatskin tanner, for example, can only hedge by selling hides and goatskin prices do not always move up or down with hide prices, although the general trend over extended periods of time is usually the same. His hedging by selling hide futures is often far from being perfect, but it is vastly safer than no hedging at all.

"Even the tanner of light native cow hides does not achieve a perfect hedge by selling hide futures. Although light native cows constitute the basis grade for trading on the exchange, the grade for trading purposes varies with the relative market values of the various tenderable grades. Since the deliverable grade is at the option of the seller of the contract, it automatically becomes the grade that costs least to make delivery. When light native cows are selling for less than other tenderable grades, they automatically become the grade to be delivered. When butt-branded steers are selling for less than any other tenderable grade, they automatically become the grade to be delivered. Frigorifico hides can be delivered on a contract and a premium charged. Ordinarily Frigorifico hides have too high a market value to be considered as deliverable grades, but right now (October, 1940) the present world crisis has made Frigorificos the grade to be delivered.

"Tanners naturally look upon butt-branded steers as more valuable than light native cows and usually they do sell at a higher price. However, changing demands have forced butt-branded steers to sell for less than light native cows during at least five different periods in the last thirty years and that condition exists at the present time. Fig. 86 shows the variation in cents per pound by which the price of butt-branded steers has exceeded the price of light native cows over the past thirty years. Actual prices can be seen by comparing the values in Fig. 86 with the average values shown in Fig. 83.

"When a tanner sells a hide futures contract, the logical deliverable grade may thus change during the life of the contract and this prevents perfect hedging regardless of the grade of hides being tanned by the seller of the contract. This has often been used as an argument against the desirability of hedging, but it does not require a mathematical genius to show that the present method of hedging with all of its imperfections is far safer than no hedging at all.

"In considering the imperfections in hedging just cited, it seems to the writer that a wonderful opportunity is afforded the hide exchange to remove some of these imperfections by substituting for the *fixed* differentials given in Section 828 variable differentials based upon variations in the relative market values of the different tenderable grades.

Making the Profit

"The world is now passing through a crisis that is upsetting at least temporarily many normal processes. Conditions existing in the hide market today are abnormal in many respects and so for our illustration we shall consider only those conditions which usually exist and not those that are with us temporarily as an indirect result of the world crisis. When hides are sold for future delivery, the price is usually increased by 10 points (0.10 c per lb.) for each month of the life of the contract This represents what are known as carrying charges and includes storage charges

on the hides, insurance, interest and handling charges. On the basis of hides at 10c, this amounts to 12 percent per year on the value of the hides.

"Since the tanner sells hide futures solely for the purpose of hedging and with no intention of making delivery, he has no carrying charges on the contract sold, but he receives the regular carrying charges as a bonus. This amounts to \$480.00 per unit contract of 40,000 lbs. of hides per year. Against this bonus, he must pay brokers' commissions on each transaction. In routine hedging, he would sell and clear each contract twice each year, making four separate transactions per contract. When hides were selling below 10c, the broker's commission on each transaction would cost him \$7.50, making a total cost of \$30.00 per contract per year. When hides were selling above 10c, the broker's commission on each transaction would cost him \$10.00, making a total of \$40.00 per contract per year. Deducting these from his bonus of \$480.00 leaves him a net profit of either \$440 or \$450 per contract per year. On the basis of 10c hides, this amounts to 11 percent to $11\frac{1}{2}$ percent on the value of the hides annually. For many tanners, this amounts to far more than their profits on all tannery operations put together.

"During the present crisis, these carrying charges have sometimes amounted to only one-third of their normal value and sometimes have been non-existent, but they form a normal part of the transactions on the futures markets.

The Tanner as a Seller of Hide Futures

"The average tanner should never buy hide futures except to clear contracts that he has sold. As long as he has an inventory of hides and leather, he must keep the value of its raw-stock content sold to avoid virtual ownership with its concomitant speculation. Sometimes a tanner sells leather for future delivery and sometimes even before he has purchased the hides with which to make it. In this case, he should deduct the futures sale of leather from his inventory. If this leaves him with a negative inventory, he should then buy futures to balance, but this condition is so rare that it will hardly interest the average tanner. The fundamental rule, which takes care of all cases is simply this: The market value of contracts sold should always equal the market value of the raw-stock content of the inventory.

The writer is indebted to Mr. Henry Dietrich, of Armand Schmoll, Inc., New York, for giving him many ideas about trading on the Exchange."

Selection of Hides for Specific Types of Leather

For each kind of leather, some types of raw stock are better suited than others. Under exceptional circumstances, a tanner might use almost any type of raw stock to make almost any type of leather, even though the resulting product might be far from the best obtainable. For example, a tanner would not buy heavy steer hides to make upper leather for women's shoes, but it is physically possible to split such a hide to women's weight and make the shoe-upper leather; it would not be durable leather because of the necessary degree of splitting and it certainly would not be economical. In selecting the type of raw stock to make any given type of leather, the tanner must consider both suitability and the market price of the raw stock. A type of raw stock that best filled his needs under one set of circumstances might not be best under another set of circumstances.

Although no rigid rules can be laid down for all circumstances, it is helpful to the tanner to have a list of types of raw stock that have been used to make each common type of leather as a first guide when attempting to produce some type of leather for the first time. Such a list is given in Table 20. It would be futile to attempt to list every type of leather that has ever been made, and the tanner

may often find types of raw stock to use to best advantage that are not listed in the table for the given type of leather.

Table 20. Various Types of Leathers and Types of Raw Stock That Have Been Used to Make Them.

Types of Leathers

Alligator

Antelope

Apron

Automobile

Bag

Baseball-glove

Baseball

Baseball-mitt

Baseball-shoe-upper

Basketball (molded ball) Basketball (sewed ball)

Bellows Belting

Billfold

Bookbinding

Boxing-glove Bridle

Brief-case

Buckskin Buffalo

Cabretta

Caddie-bag Cap Case Catgut

Chamois Collar

Cordovan Counter

Deerskin Diaphragm

Drumhead

Elk

Football-helmet

Football Garment

Gasket

Gear

Glazed-kid Glove (dress)

Glove (work)

Types of Raw Stock

real alligator skins or light cows and calf skins

(embossed).

goatskins, sheepskins and calfskins (suède

finish).

light steer hides and light cow hides.

bull hides, steer hides, spready cow hides and

cattle-hide splits.

light and heavy native steer and cow hides. kipskins, light native cow hides and horse

fronts.

kipskins and horse fronts.

light native cow hides and horse fronts.

kangaroo skins, wallaby skins, calfskins, kip-

skins and East-India kipskins. kipskins and country cow hides. ex-light and light native steers.

pickled sheepskins and sheep skivers.

heavy native steers.

calfskins, hog skins, sheepskins, hair-seal skins and many others.

goatskins, sheepskins and skivers, calfskins and many others.

pickled sheepskins. light native steer hides.

light native steer and cow hides.

real buckskin or light native cow and kipskins.

various imported buffalo hides.

straight-haired Chinese sheepskins. light native cow hides and many others. pickled sheepskins and many others. light native steer hides and cow hides.

sheep intestines. pickled sheepskins.

light and heavy native steer hides and cow

hides. horse butts.

hog strips and country cow hides.

deer and elk skins. sheepskin skivers.

sheepskins, calf slunks and other types un-

tanned.

real elk skins or (usually) light native steer

hides or cow hides. light native steer hides.

light native steer hides. pickled sheepskins, horse fronts, light native

cow hides, kipskins and calfskins. sheepskins, country cow hides, kipskins, calf-skins, splits and many others.

bull hides

imported goatskins and kid skins.

goatskins, kidskins, sheepskins, cabretta skins. ostrich skins, deerskins, hogskins, peccary skins, and many others.

country cow hides, horse fronts and many

others.

Table 20-Continued.

Types of Leathers Gold-beater's skin Golf-grip Gusset Hairon (textile)

Harness

Handbag

Hathand Hat

Hydraulic Insole Kangaroo Lace

Lining

Lizard

Loom-strap

Luggage

Mechanical Meter

Moccasin

Mocha Morocco ()oze Organ-pipe Ostrich

Packing Parchment Patent Piano

Pigskin

Pin-seal

Pneumatic Pocketbook

Portfolio Razor-strop Reptile Roller Round-belting Saddle Sealskin Seat-cover

Shark Shearling Types of Raw Stock

blind gut of ox. country cow hides, kipskins and calfskins. pickled sheepskins.

extra-heavy French and Italian steer hides. light native steer and cow hides, kipskins, calfskins, goatskins, sheepskins, ostrich skins,

hogskins and many others. light and heavy native steer hides and bull hides.

pickled sheepskins and calfskins.

pickled sheepskins, goatskins, calfskins and others.

light and heavy steer hides and cow hides.

hog strips and country cow hides.

Australian kangaroo skins.

East-India kinskins, light steer and cow hides, kinskins and calfskins.

goatskins, cabretta skins, pickled sheepskins, calfskins and hogskins.

real lizard skins or light cowhides, kipskins, calfskins, and goatskins (embossed).

extra-heavy French and Italian steer hides and Chinese water-buffalo hides.

light steer and cow hides, buffalo hides, alligator skins, shark skins, hogskins and many

bull hides.

pickled sheepskins, sheepskin skivers, calfskins and others.

pickled sheepskins, shearlings, deer skins, light cow hides, calfskins and others.

Mocha goatskins.

goatskius and sometimes sheepskius.

calfskins.

blind gut of ox

real ostrich skins or light cow hides, kipskins and calfskins (embossed).

sheepskins and splits.

sheepskins, calfskins and slunks, untanned. all types suitable for shoe upper leather.

deerskins, elk hides, moose hides, goatskins, sheepskins, light cow hides and calfskins.

hogskins, peccary skins and light cow hides and calfskins (embossed).

hair-seal skins or calfskins and goatskins (embossed).

sheepskin skivers.

hair-scal skins, calfskins, goatskins, sheepskins, reptile skins and many others.

light native steer and cow hides and others.

hogskins, horse butts and cow hides. real reptile skins or calfskins (embossed).

high quality lambskins and small calfskins. heavy steer hides.

light native steer hides, and heavy hogskins.

hair-seal skins.

light native steer and cow hides, kipskins and calfskins. shark skins.

sheep and lambskins tanned with wool on.

Table 20—Continued.

Types of Leathers

Shoe-upper (men's dress)

Shoe-upper (women's dress)

Shoe-upper (workmen's) Skirting

Skiver Slipper

Sole leather (chrome-retanned)

Sole leather (chrome-tanned)

Sole leather (finders' vegetable-tanned)

Sole leather (manufacturers' vegetable-tanned)

Sole leather (white alumtanned)

Stirrup Strap

Suède

Suspender-strap

Textile

Upholstery

Valve Volley-ball Waist-belt

Wallaby Wallet

Washer Welting Whip

Wrist-watch strap

Types of Raw Stock

calfskins, kipskins, light native cow hides, goatskins, kangaroo skins, horse butts, hog-skins and others.

goatskins, kidskins, light calfskins, slunks, sheepskins, cabretta skins, hair-seal skins, reptile skins, ostrich skins and many others. country cow hides, horse hides and splits.

light and heavy native steer hides.

sheepskins.

sheepskins, calfskins, deerskins, rabbit skins, goatskins, cabretta skins, cow hides and

light steer hides and light and heavy cow

bull hides, light steer hides and light and heavy cow hides.

heavy bull and steer hides.

bull hides and light and heavy steer hides.

light steers.

light native steer hides.

light native steer hides and light and heavy native cow hides.

best from calfskins, calf slunks and kangaroo skins; cheaper grades from light native cow hides, kipskins and sheepskins. light native cow hides, kipskins, calfskins,

horse fronts and hogskins.

light and heavy native steer hides and cow

bulls, heavy native steer hides and cow hides and splits.

light cow hides, calfskins and sheepskins.

light cow hides, kipskins and calfskins. light native cow hides, kipskins, calfskins, shark skins, hogskins and many others.

Australian wallaby skins.

hair-seal skins, calfskins, goatskins, sheepskins,

hogskins, cow hides and many others. cow hides and splits, calfskins and sheepskins.

cow hides and hog strips. cow hides, calfskins, goatskins, sheepskins and shark skins.

cow hides, calfskins, hair-seal skins, ostrich skins, hogskins, reptile skins and many others.

References

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Chapter 7

Handling Raw Stock as Received at the Tannery

The preceding six chapters represent the minimum that a modern tanner should know before purchasing hides and skins for making specific types of leather. Having purchased them, he must be prepared to receive them and know what to do with them upon arrival.

The Hide House

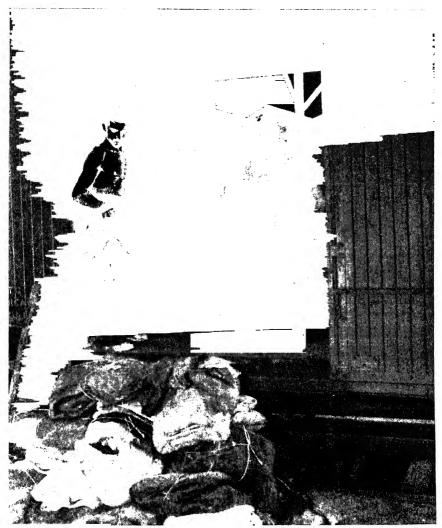
A hide house may consist merely of a cool cellar where raw stock may be kept for a week or more without danger of spoiling, or it may be an elaborate building including cold-storage facilities. In any case, it should provide ample storage space with easy access to all piles of raw stock and allow freedom of movement for workmen to open hide bundles, examine and grade the stock and make it into packs for the tannery according to kind and quality. It should also provide space for recuring when this is deemed advisable. It should be kept cool and scrupulously clean at all times. It should be so arranged as to allow frequent cleaning and disinfection of floors and walls. If cold-storage facilities are provided, raw stock can be stored for very long periods of time.

Immediately upon arrival at the tannery, the raw stock should be moved to the hide house. Fig. 87 shows hide bundles being weighed and taken from freight car as received at the tannery. If the stock has been imported from restricted countries, the regulations of the Bureau of Animal Industry given in Chapter 4 should be followed explicitly. In the case of domestic green, salted stock, each bundle should be opened and the hides or skins examined carefully for damage as soon as possible after they reach the hide house. If claims are to be made for damages or inferior quality, the sooner they are made the better.

It is good practice to keep a careful record of each purchase of hides or skins and to assign to it an identifying number or letter. Upon opening each bundle, some tanners have each hide or skin weighed, and then stamp in the head or tail the purchase number or letter and the weight. If a hide is later to be cut into sides, the designating stamp is placed on both sides of the backbone line. Each stamp is made of steel with the letter or number formed by sharp teeth, which leave an identifying mark that is still sharply defined on the finished leather. By using one letter and two numbers to represent a purchase order, 2600 purchase orders can be covered before the designations begin to repeat, and this usually means 2600 carloads of hides or skins. The stamps are usually set into a holder capable of taking three to five stamps; this forms part of a hammer like that shown in Fig. 88 with which the stamping is done. Many tanners use a foot-power stamping machine like that shown in Fig. 89.

Later on in the tannery, the necessary reassortments into packs may cause hides or skins from different purchase orders to be mixed, but the tanner with a little pocket notebook of purchase order numbers can identify any hide or skin by its identification number. For example, he may pick up a hide after tanning and note the stamp 97G52 in the tail. He knows at once that it was part of the purchase order designated 97G and that it weighed 52 pounds upon arrival. When

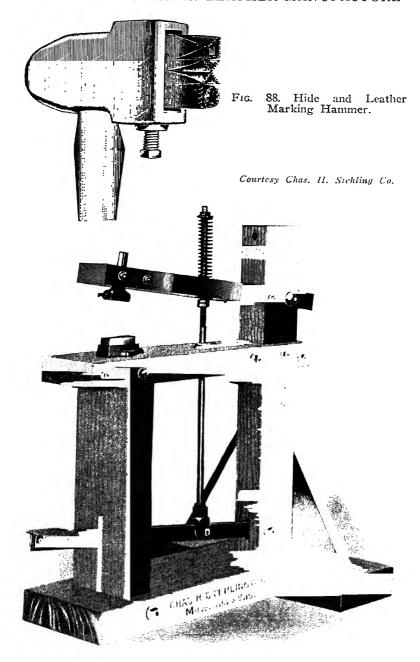
the leather is ready for sale, he will get yield values for all stock stamped 97G as well as quality records. In this way he builds up a huge fund of information relating yield and quality with his purchases of raw stock and acquires experience in selecting his sources of raw stock that he could never find in books.



Courtesy Lindicott-Johnson Corp.

Fig. 87. Hide Bundles Being Weighed and Taken from Freight Car as Received at the Tannery.

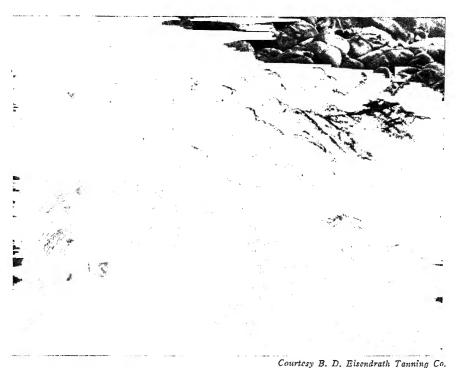
The stamp is usually placed close to the edge of head or tail so that it can be cut away from the finished leather after final assortment with negligible loss. Sometimes this stamping is done only at the tail edge, leaving the head edge for



(16, 89. Foot-Power Hide and Leather Stamping Machine.

other identification stamps to indicate special procedures in any of the operations of the tannery.

After all the bundles from a given shipment have been opened and examination has been completed, piles of the raw stock are made according to kind, weight, damage and general quality, so that each pile contains as nearly as is practical the same grade and weight of stock. All pieces in any one pack entering the tannery should be as nearly alike as possible, as this makes for uniformity of results in each operation.



Courtesy B. D. Eisenarath Lanning

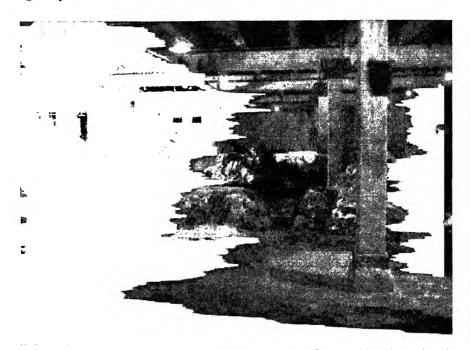
Fig. 90. Bundles of Calf Skins as Received at the Tannery.

In examining the incoming stock in the hide house, the workmen should be alert to note anything requiring prompt attention. If there are signs of putre-faction, the stock should either be rushed through the tannery quickly or be sent to be recured at once. In recuring, the object is to get plenty of clean salt into every part of every hide just as quickly as possible. If portions of a hide have dried out, the dried areas should be wet thoroughly with saturated salt solution and allowed to lie in the piles to condition. If there is any evidence of heating when the bundles are opened, the stock should be spread out to cool. The inspection of incoming hides is so important that the tanner should either do it himself or trust it only to a man of proved experience.

Fig. 90 shows a shipment of bundles of calf skins as received at the tannery. Fig. 91 shows the men at work on calf skins in a hide cellar, grading them into

piles according to their suitability for given qualities of stock and taking care of those requiring prompt attention.

There may be many reasons for storing calf skins before putting them through the tannery, if a tanner has the facilities for keeping them properly and the funds necessary to carry them. He may have an opportunity to purchase stock advantageously that he knows he will need at some future time. In Chapter 1, it was



Courtesy The Ohio Leather Co.

Fig. 91. Workmen Selecting Calf Skins in a Hide Cellar.

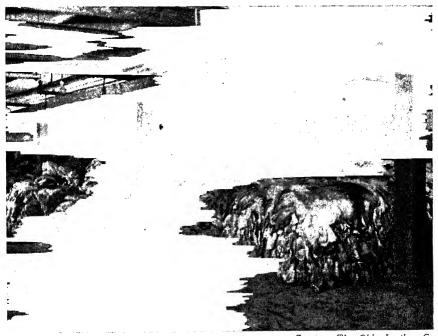
pointed out that domestic calf skins from animals slaughtered in hot, summer weather produce much finer leather than those from animals slaughtered in cold, winter weather, and the reason for this was given. It is thus greatly to the advantage of a calfskin tanner to get all his raw stock for the year from summer kill, and he may have to have cold-storage facilities to do this economically. When stock is moved into cold storage, it is important to dissipate its heat before it is left there in its final piles. As hides and skins are powerful insulators against heat and cold, the pieces in the middle of large piles would not cool in storage for a very long time, unless they were frequently turned over to allow each individual piece to become cold. Chemical and bacterial reactions in the middle of a large pile which remained warm would produce heat which might gradually ruin the whole pile. It is thus important to repile the stock frequently until every piece is cold before allowing any piles to stand for very long periods.

In cold storage, it is important to guard against excessive drying of the exposed portions of a pile, because dried areas cannot be wet back in the tannery nearly so readily as the undried areas, and poor leather lacking in uniformity would result.

Fig. 92 shows piles of calf skins in cold storage. Fig. 93 shows mechanical equipment for moving raw stock in a modern hide house.

Most of the goat skins tanned in this country are imported as dried skins, and these do not require cold-storage facilities for safe keeping. However, it is important to guard them against water while in storage. If they are allowed to become wet, chemical and bacterial reactions set in which liberate heat which would destroy them, if not stopped in time. The same may be said for any dried stock.

If kept cool, pickled sheepskins can be kept for a very long time without damage, but when warm they may deteriorate rather rapidly. Before leaving them for a long time in cold storage, it is important to make sure that the piles are cold throughout. It is also very important to guard them against water which might wash away some of the salt and subject them to rapid destruction by the acid which they contain. Pickled stock as received at the tannery has already been unhaired, and so does not go through the same operations as stock received with the hair on.



Courtesy The Ohio Leather Co.

Fig. 92. Calf Skins in Cold Storage.

In this and the next chapter, we shall consider tannery operations only of green, salted and dried stock having the hair still on it, and from which the hair is to be removed.

In the hide house, individual packs of hides or skins are made up for entry into the tannery. Each pack contains individual pieces as nearly alike as is practical. Although individual packs may vary in size, it is desirable to have them as uniform as possible. When the vats in the beamhouse have a total capacity of 2500 gallons,

it is common practice to make up packs of green, salted stock to 5000 lbs. each and dried stock to 2500 lbs. each.

Trimming

In flaying calfskins, the ears, hoofs, and tails are often left on the skins, and these are first removed by the operation known as trimming. Fig. 94 shows men at work trimming calfskins. Each skin is laid over a rounded wooden beam, and the workman, using a two-handled, two-edged, rounded knife cuts away those portions that have no value in leather making. These trimmings are sold for manufacture into gelatin. Calfskins are usually weighed into standard packs after trimming.

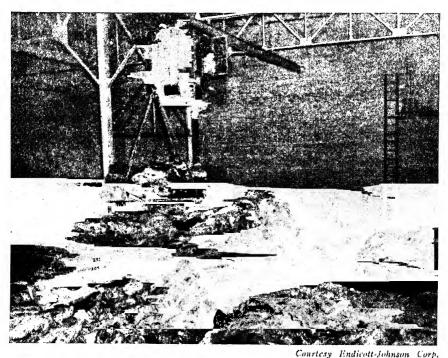


Fig. 93. Mechanical Equipment for Moving Raw Stock in Modern Hide House.

For packer hides cut to correct or standard pattern, this preliminary trimming is not necessary, although some trimming is usually done after the stock has been unhaired. Dried stock is not trimmed until after it has been soaked.

Soaking

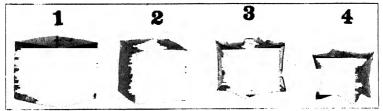
The first major operation after the stock enters the tannery is soaking. This operation has two purposes: the first is to wash from the stock the water-soluble material that might otherwise cause difficulties in later operations, and the second is to cause the fibers to absorb water to restore them to their normal sizes and shapes. Although the purposes are simple, their accomplishment is often fraught with serious difficulties.



Courtesy B. D. Eisendrath Tanning Co.

Fig. 94. Workmen Trimming Calfskins on the Beam.

Besides the salt used in curing, the water-soluble matter in the raw stock contains soluble proteins from the blood and lymph, some of which are coagulable. The soluble proteins extracted by water furnish excellent food for bacteria, which multiply at an enormous rate and constitute a menace to the stock during the soaking period. The removal of these soluble proteins during soaking is complicated by the epidermis, which is not permeable to them, and by occasional layers of adipose tissue on the flesh side, through which they can pass only with difficulty.



Courtesy Eastman Kodak Co.

Fig. 95. Four Stages in the Drying of a Cube of Gelatin Jelly.

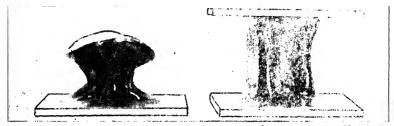
During the drying of hides and skins, the fibers suffer a change of shape, as well as of size, depending upon the resistance to shrinkage in any direction, the rate of drying and many other factors. In curing, similar changes occur, although



Courtesy Eastman Kodak Co.

Fig. 96. Three Stages in the Drying of a Sphere of Gelatin Jelly.

they are not nearly so marked as in complete drying. Physically, a hide fibril may be likened to a thread of gelatin jelly. Studies of gelatin jellies, which can be carried out simply, often reveal facts about hide fibers and fibrils that could otherwise be obtained only with extreme difficulty. A better appreciation of the changes in size and shape of hide fibers during drying or curing can be obtained by studying the results of some experiments on gelatin jellies by Dr. S. E. Sheppard of the Eastman Kodak Co.



Courtesy Eastman Kodak Co.

Fig. 97. Two Cylinders of Gelatin Jelly Dried with One and Two Paces, Respectively, Adhering to Rigid Surfaces.

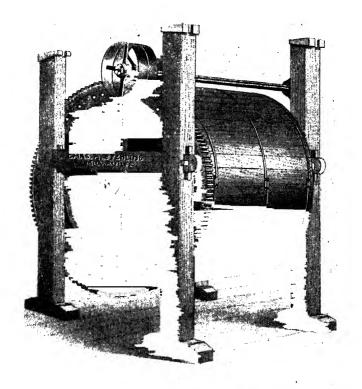
Fig. 95 shows four stages in the drying of a cube of 20 per cent gelatin jelly which was freely suspended in the air. No. 1 represents the original block of jelly, Nos. 2 and 3 intermediate stages in the drying, and No. 4 the dried block. At first the drying naturally proceeds most rapidly at the corners, or trihedral angles, and the faces of the cube become curved outward, as shown in No. 2, giving convex



Courtesy Eastman Kodak Co.

Fig. 98. End Views of Dried Cylinders of Gelatin Jelly Shown in Fig. 97.

surfaces under tension. This is rapidly followed by the drying and hardening of the edges, forming a rigid framework, so that the bulk of the jelly now behaves as though suspended inside of a rigid wire frame. The faces now gradually recede and the edges become somewhat incurved until a sort of inner cube is formed with connected flanges reinforcing it, any cross-section through this having an I-beam structure, as though the drying proceeded in a manner developing the greatest resistance to stress. The flange-like edges appear to form sections of hyperboloids with a common focus at the center of the cube. Fig. 96 shows three stages in the drying of a sphere of gelatin jelly. Even here the drying is not uniform, but the surface becomes puckered and wrinkled.



Courtesy Chas, H. Stehling Co.

Fig. 99. Typical Drum Used for Washing Hides and Skins Before Soaking.

The dried forms of two cylinders of gelatin jelly are shown in Fig. 97 and their end views in Fig. 98. One base of the first and both bases of the second cylinder were allowed to adhere to rigid surfaces during the drying. The shrinkage in area of these bases being prevented, the reduction in volume had to be compensated by greater shrinkage in other directions. In the drying of a thin coat of gelatin jelly on a glass plate, the shrinkage takes place almost entirely in the direction perpendicular to the plane of the glass surface.

Upon soaking dried blocks of gelatin in water, the swelling proceeds in the

direction counter to that followed during drying and the blocks tend to assume the shapes and sizes they possessed before drying.

During the drying of skin, the distortion of shape suffered by the insoluble protein constituents are further complicated by the tendency for the fibers to cohere.

Soaking Green, Salted Calfskins

Before discussing the factors which may complicate the soaking operation, the complete operation will be described for high-grade, green, salted caliskins under conditions where these complications are at a minimum. The procedure follows:



Courtesy Endicatt-Johnson Corp.

Fig. 100. Putting Hides into Large Washing and Conditioning Drum from Upper Floor.

Put a pack of calfskins into a wash drum, like that shown in Fig. 99. This drum is made of cypress wood, has an outside diameter of 8 ft. and a width of 5 ft., 4 in. and rotates with a speed of 17 revolutions per minute. It is equipped with a water pipe allowing a heavy flow of water to pass over and through the skins while the drum is revolving. The inside of the drum is equipped with wooden pegs which pick up the stock and allow it to drop back repeatedly while the drum is running. The wash water flows out through the open side of the drum. The stock is washed in running water in this drum until the outflowing water looks clear and no longer bloody and dirty from material being washed from the skins. The time required to reach this stage is about 5 minutes. Excessive running of the stock at this

stage should be avoided because it may produce distortions in the skins that appear in the final leather as a looseness of structure.

Figs. 100 and 101 show a large drum used for washing and conditioning heavy hides as received. The stock is put into the drum from the upper floor, as shown in Fig. 100 and removed on the lower floor, as shown in Fig. 101.

After washing, throw the calfskins, one by one, into a vat of clean water at a temperature of 52 °F. and leave them there over night. Under favorable conditions, the temperature of the water will rise only about 2 ° over night. Next morning haul out the stock and *flesh* it on a good fleshing machine, to be described



Fig. 101. Removing Hides from Large Washing and Conditioning Drum on Lower Floor.

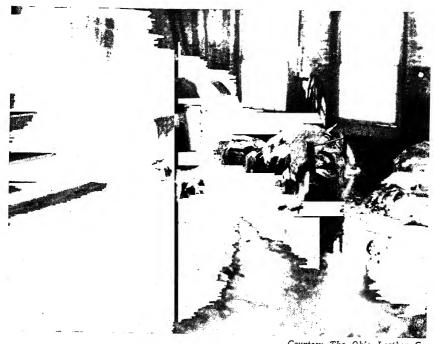
later, and then throw the skins back, one by one, into a vat of fresh, clean water at a temperature of 52 °F. and leave it until next day. Then haul out the skins again and throw them, one by one, into a third vat of fresh clean water at a temperature of 52 °F. and leave them there over night. Next day, haul out the pack and move it to the department for unhairing. If warmer water is used, the time of soaking must be shortened.

Fleshing

Fig. 104 shows a modern fleshing machine. It consists essentially of two long rolls, one of corrugated metal and the other of rubber; these grip the skin, with a pressure that can be regulated, and draw the flesh side of it across a revolving cylinder set with spiral blades. The bladed cylinder can be seen in the picture between the two rolls. With the machine running, the workman inserts a skin to a

depth of more than one-half of its length between the two rolls and with the flesh side under and facing the bladed cylinder. He then steps on the lever and the two rolls come together and force the skin outward. At the same time the revolving bladed cylinder presses on the flesh side of the skin backed by the rubber roll and cuts away the adipose and areolar tissues that constitute the flesh of the skin. All pressures on the machine can readily be adjusted by the operator. The machine is also equipped with a grinder enabling the operator to keep the blades on the cylinder sharp.

The writer's object in fleshing calfskins between soakings is to allow the fibers sufficient contact with water to bring them nearly to their normal sizes and shapes



Courtesy The Ohio Leather Co.

Fig. 105. Workman Operating a Fleshing Machine in a Calf Tannery.

so that the fleshing may be done reasonably uniformly, and yet to have the fleshing done before soaking is completed to enable most of the soluble proteins to be removed before the unhairing operation. Soaking before liming facilitates the liming operation and makes it more uniform. In Europe, it appears to be customary not to flesh until after liming; most tanners of dried goatskins flesh after liming.

Fig. 105 shows an operator fleshing calfskins in one calf tannery and Fig. 106 shows a more intimate view of this operation in another calf tannery.

The writer's use of a temperature of 52° F. and a soaking time of 3 days for green, salted calfskins had its origin in a calf tannery using well water that had a constant temperature all year round of 52°F. At this temperature, it was found necessary to soak the skins for a minimum of 3 days to bring the fibers back to

their normal sizes and shapes. It was also found that at 52 °F. under these conditions of soaking, there was no measurable bacterial damage done. It was found that the time of soaking could be shortened by raising the temperature to 60 °F., but bacterial damage became appreciable and had to be guarded against. In tests on millions of skins, it was found that a temperature of 52 °F. and a soaking time of 3 days were ideal. If the soaking time was shortened at this temperature, the effect upon the fibers could be observed in the finished leather.

Before proceeding with descriptions of other types of raw stock, it seems desirable to acquaint the reader with the effects of impurities present in natural waters, with bacterial action, with the use of antiseptics, and with the concept of pH value.

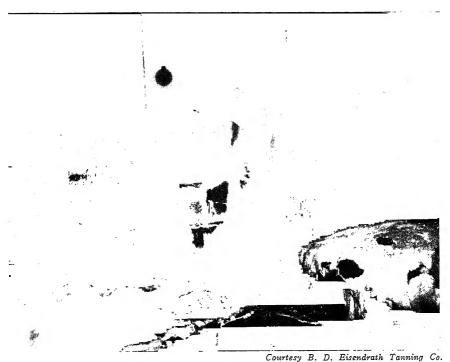


Fig. 106. Close-up of the Operation of Fleshing Calfskins.

Water

Much has been written of the importance of a plentiful supply of pure water for a tannery. For most tanneries, the supply of water must be plentiful and it must not contain impurities that are injurious. Because of the complex nature of his business, nearly every tanner runs into occasional difficulties for which he is unable quickly to determine the cause. At such times, tanners have been known to suspect that their troubles were due to the hardness of the water used, and to install expensive water-softening systems, only to find that no improvement resulted from softening of the water. All tanners should have their water supplies analyzed at intervals and be thoroughly familiar with their content of foreign materials, to guard against the possibility of dangerous impurities harming their stock; but

the writer's experiences indicate that damage from impurities in natural waters is rather rare. He once had available in a calf tannery two large supplies of water, one a well water that was considered hard and the other a lake water that was considered fairly soft. Their analyses are given below:

	lake water (parts per	well water million)
Total solids	148	331
Temporary hardness	116	250
Calcium	33	50
Magnesium	10	30
Iron	0.1	0.1
Aluminum	1.0	1.4
Chloride	8	11
Sulfate	14	79
Silica	8	8

Comparisons were made with these two waters in every operation in the tannery where water was used. In all the beamhouse operations, the results were identical. In chrome tanning, there was no difference except when washing the chrometanned stock with running water for a long period, when the well water effected a greater degree of neutralization of the acid in the stock than the lake water. In vegetable tanning, there was no difference. In fatliquoring, there was a measurable difference; the well water caused a greater precipitation of calcium and magnesium soaps, which are undesirable. In dyeing, the well water required a greater addition of formic acid. In fatliquoring, the difference between the two waters could easily be overcome by adding a small percentage of Calgon, or sodium metaphosphate, which prevents the precipitation of calcium and magnesium soaps; only just enough is required to combine chemically with the small proportions of calcium and magnesium present in the water.

If appreciable percentages or iron are present in water, discoloration may occur when it is used with vegetable tanning materials; but even here small proportions of Calgon will prevent discoloration by combining with the iron so vigorously that none is left available to combine with the tannins. The composition of water used in the tannery is very important, but decisions to change the composition should be made only after the effect of each constituent has been studied in relation to the operation for which it is to be used. For most natural waters used in soaking hides and skins, the temperature of the water is more important than its chemical composition.

Bacteria

Hides and skins must be protected against the damaging action of bacteria from the time of the slaughter of the animals until after the hides are tanned. Hides and skins consist essentially of protein material, and the common action of bacteria on proteins is known as putrefaction, which means making putrid, or rotten. In this action, the proteins are decomposed, with formation of foul-smelling reaction products. The fundamental action of tanning is to render hides and skins imputrescible, which means resistant to putrefaction. Bacteria are a form of plant life, which includes molds, yeasts and mildews, so small that they can be seen only with the aid of a powerful microscope, for which reason they are classed as microörganisms. Tanneries abound in microörganisms, which have been called the tanners' invisible friends and foes. Although these microörganisms can do but little direct damage to the stock after it has been tanned, they can still live and

reproduce in wet leather. Molds and mildews can render leather unsightly, and must therefore be guarded against even after tanning. This subject will be discussed in Chapter 14.

The four great subdivisions of plant life are the *Spermatophyta* or seed plants, the *Bryophyta* or moss plants, the *Pteridophyta* or fern plants, and the *Thallophyta*, which include bacteria, yeasts, and molds, the common microörganisms of the tannery.

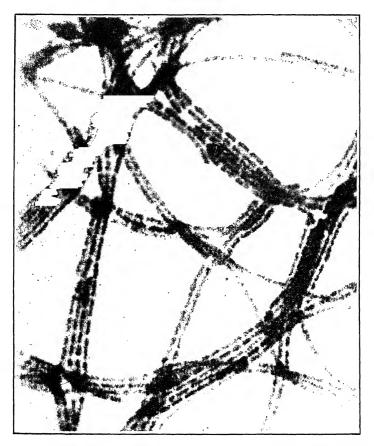


Fig. 107. Long Chains of Rod-shaped Bacilli from Tannery Soak Water.

Magnification: 1600 diameters.

The *Thallophyta* are simple plants which are never differentiated into roots, stems, and leaves. Those which contain chlorophyll are the *Schisophyta* or bluegreen algæ; those unicellular plants which multiply by cell fission only and contain no chlorophyll are known as the *Schisomycetes* or bacteria. Those unicellular or multicellular plants which multiply by means other than simple cell fission and contain no chlorophyll are the *Fungi*, which include yeasts and molds, or mildews.

A bacterium is a plant consisting of a single cell containing no chlorophyll and reproducing only by cell fission. Bacterial cells are usually one of three shapes,

spheres, straight rods, or bent rods. A spherical cell is a *coccus*; a straight rod a *bacillus*; and a bent rod a *spirillum*. Bacteria are so small that it is customary to take as the unit of measurement the micron, which is one-thousandth of one millimeter. The dimensions of common bacteria range from 0.5 to 10 microns. A bacterium of average size might have a volume of one cubic micron, so it would take one trillion bacteria to fill the space of one cubic centimeter. Of all the liquors in the tannery, those most heavily laden with bacteria are the bate liquors and the highest count ever obtained in the author's laboratories of a bate liquor was slightly more than one billion per cubic centimeter. This tremendous number occupies only about 0.1 per cent of the volume of the liquor and probably weighs not more than one milligram.

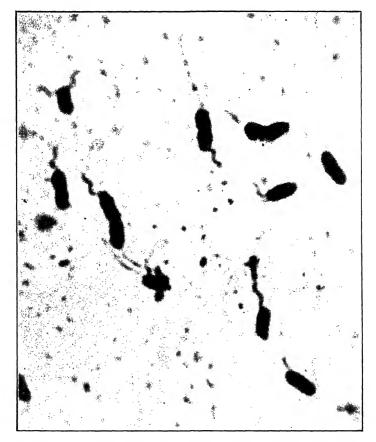


Fig. 108. Rod-shaped Bacilli with Flagella from Tannery Soak Water.

Magnification: 2700 diameters.

Bacteria multiply by a process of cell fission. The cell grows until one dimension has practically doubled, when it separates into two individual cells. Some bacteria produce spores in the course of their growth. The spore is usually much more resistant to destruction than the parent cell and the theory has been advanced

that spore formation is not a method of multiplication, but rather a protection against unfavorable environment.

During the multiplication of bacteria, the cells do not always become detached from each other, but often cling together forming characteristic groups which serve to identify them. Such group formation of long chains of rod-shaped forms is shown in Fig. 107, which is a photomicrograph of bacilli found in a used tannery soak water. The cells simply become elongated and then subdivide, but remain attached forming long chains. When spherical cells divide in this manner, forming long chains, they are called streptococci. When they form irregular clusters, they are called staphylococci and when they show a tendency to remain united in pairs, they are called diplococci. Spirilla very rarely occur in groups.

Some bacteria possess organs of locomotion known as flagella. These are extremely thin protoplasmic threads and serve to propel the organism by means of a corkscrew motion. The bacilli shown in Fig. 108 are equipped with flagella. For any particular organism the size, number and arrangement are characteristic and serve to identify it.

Buchanan has made an interesting calculation of the rate of growth of bacteria under ideal conditions. Probably most of the more active bacteria can grow to their full size and divide to form two individuals within thirty minutes. If it is assumed that this process continues for two days the number of bacteria growing from one initial cell will be 2 raised to the 96th power and their total weight more than one trillion tons. Of course no such bacterial masses could ever be formed because of the disappearance of available food and the production by the bacteria of substances hindering their own development.

It is very important to the tanner to appreciate just how the bacteria do their damage. They are not equipped with any means for biting into the protein tissues and destroying them that way; their action is much more subtle. They can utilize as food only material that is already in solution. The dissolved foods diffuse through the cell walls of the bacteria and the bacteria reproduce. In the course of their reproduction, chemical substances known as *ensymes* are formed. These enzymes are soluble in water and diffuse through the cell walls of the bacteria into the surrounding water. When the enzymes come into contact with the insoluble protein of the hide fibers, they cause a chemical reaction to take place between the protein and water. This is known as *hydrolysis*, because the water takes part in the chemical reaction. The protein is broken down into water-soluble products, which diffuse through the cell walls of the bacteria, providing them with food for further reproduction and the production of more enzymes to do further damage to the hide fibers. The action of enzymes will be discussed in greater detail in Chapter 8 in connection with the *bating* operation.

In putrefaction, the real damage is done by the enzymes which the bacteria produce and secrete in the course of their own reproduction. In order to prevent any appreciable bacterial damage in soaking, it is thus necessary to do one of three things: (1) destroy the bacteria, (2) create a condition unfavorable to their reproduction and secretion of enzymes, or (3) create a condition unfavorable to the activity of the enzymes.

Antiseptics

One of the most powerful agents known to destroy bacteria is the chemical element *chlorine*. At ordinary temperatures and pressures, chlorine is a greenish-yellow, poisonous gas with a suffocating odor. Under pressure, it can be condensed to a liquid, and it is usually sold in this form under pressure in metal

cylinders. In order to use it conveniently in treating tannery soak waters, it is important to have special equipment like that used by municipalities in chlorinating their drinking-water supplies. The writer has successfully used the chlorinator made by Wallace & Tiernan Co., Inc., Newark, New Jersey and shown in Fig. 109. The chlorine cylinder and a water line are attached to the chlorinator; by means of a system of controls any desired amounts of chlorine dissolved in water can be delivered to the soaking vats.

In connection with the method of soaking green, salted calfskins given above, the writer made a quantitative study of the effects of chlorination. Using 44 parts of chlorine per million of soak water, or about 1 lb. to 2728 gals. of water, the average bacterial count after soaking for 24 hours was reduced from 12,000,000 to only 28,600 per cubic centimeter, a decrease of about 99.8 per cent. However, when the temperature of soaking was maintained at 52 °F., no bacterial damage could be detected on any of the stock regardless of whether or not chlorine had been used. But when higher soaking temperatures were used, marked bacterial damage occurred which could be prevented entirely by the use of 500 parts of chlorine per million parts of water, added before putting the raw stock into the water. Larger amounts of chlorine than this should never be used except under the most careful control, because excessive amounts of chlorine water will damage the stock. Some tanners keep chlorinators installed in their soaking departments as a safeguard to use when conditions warrant it. Except for the initial cost of installation, chlorination provides a simple, cheap and very effective method of preventing putrefaction in the soaks, and permits speeding up the soaking by using warmer water.

If the raw stock is initially in good condition and there is a plentiful supply of cold water, the writer prefers not to use any antiseptic at all, but to maintain temperatures of the soak waters between 50° and 52°F. and to replace them as frequently as may be necessary, extending the time of soaking as long as is required to get the stock fully and properly soaked, which means a minimum of 3 days.

There are many effective antiseptics other than chlorine that may be used without having any special installation, such as sodium bifluoride, sodium hypochlorite, parachlormetacresol, borax and even strong salt solutions, although the cost in the long run may exceed that of chlorine plus the cost of installing a chlorinator. In the case of hides and skins from restricted countries, as described in Chapter 4, either sodium bifluoride or sodium silicofluoride must be used as antiseptics in the soak water, or else the used soak waters must be sterilized.

pH Value

The making of leather involves a long series of exceedingly complex chemical reactions, but tanning as an art was highly developed thousands of years before the science of chemistry was known. Even today, most tanners have little or no knowledge of chemistry, but they are quick to take advantage of improvements in practical procedures brought about by the rapidly increasing knowledge of chemistry, even when they cannot comprehend the complex fundamental theories on which the improvement was based. Every operation in the tannery involving the use of water is enormously influenced by the acidity or alkalinity of the watery solutions used. The *pH value* of a solution is the measure of its active acidity or alkalinity.

Since this book is written for readers with no knowledge of chemistry, it would be out of place to discuss the complex theories on which the concept of pH value is based. Moreover, it is not necessary to understand this concept in order to measure pH value and control it accurately and intelligently. Just as tanners

with no knowledge of thermodynamics have learned the necessity for keeping temperatures of their liquors within certain narrow ranges by measuring them and noting the results, so they have learned the necessity for keeping the pH values of their liquors within certain narrow ranges by the same process. Most successful tanners today measure and control pH values rigidly.

In the March 12, 1932 issue of *Hide & Leather*, the writer published a paper for practical tanners on "The Mystery of pH Value" and so many claimed to be benefited by that portion of the paper dealing with the pH scale that it is repro-

duced below:

The pH Scale

"When any acid is dissolved in water, its molecules break up into smaller particles which we call 'ions'; there are always two or more kinds of ions, but one kind is always 'hydrogen ion,' which is characteristic of all acids. For example, a molecule of hydrochloric acid breaks up into one hydrogen ion and one chloride ion. A molecule of sulfuric acid breaks up into two hydrogen ions and one sulfate ion. The hydrogen ion is the active one in all acid solutions.

"When any alkali is dissolved in water, its molecules break up into ions, one of which is always a hydroxide ion, which is characteristic of all alkalies.

"A strong acid is one in which a large percentage of the molecules breaks up into ions; for example, in a tenth-normal solution of hydrochloric acid, out of every thousand molecules present 948 are broken up into ions and 52 left as undissociated molecules. Now, if we take the same concentration of acetic acid, out of every thousand molecules, only 13 are ionized and 987 remain undissociated. For this strength of acid solution, the hydrochloric acid contains 948/13 or 73 times as many hydrogen ions as the acetic acid solution, although the same total number of molecules has been added to the water. For this reason, we call hydrochloric a strong and acetic acid a weak acid. By titrating equal volumes of the two solutions, in the analysis for total quantity of acid, we find exactly the same quantity of acid in each, but the hydrochloric acid solution is 73 times as active because it contains 73 times as many hydrogen ions.

"Similarly, a strong alkali is one in which a large percentage of the molecules break up into ions in solution; for example, in a tenth-normal solution of sodium hydroxide (caustic soda), out of every thousand molecules present 929 are broken up into ions and 71 left as undissociated molecules. Now, if we take the same concentration of ammonium hydroxide (ammonia), out of every thousand molecules, only 13 are ionized and 987 remain undissociated. For this strength of alkaline solution, the sodium hydroxide contains 929/13 or 71 times as many hydroxide ions as the ammonia solution, although the same total number of molecules has been added to the water. For this reason, we call sodium hydroxide a strong and ammonium hydroxide a weak alkali. By titrating equal volumes of the two solutions, in the analysis for total quantity of alkali, we find exactly the same quantity of alkali in each, but the sodium hydroxide solution is 71 times as active because it contains 71 times as many hydroxide ions.

"The ionization percentages given are for tenth-normal solutions only; the percentage ionization varies with the concentration, being greater the more dilute the solution. When the hydrogen ions or hydroxide ions present in acid or alkaline solutions are removed from solution by neutralization, some of the undissociated molecules break up to effect a partial replacement of the hydrogen or hydroxide ions. In the case of the strong acids or alkalies, there is very little reserve of undissociated molecules to draw upon, while solutions of the weak acids or alkalies have relatively large reserves of undissociated molecules. For this reason, variations in concentration have relatively much less effect upon the activity of weak acids and alkalies than upon the activity of strong ones.

"Ions are electrically charged atoms or groups of atoms and are always associated with other ions of opposite charge of equivalent value. In a solution of hydrochloric acid, each hydrogen ion is associated with a chloride ion. Each hydrogen ion possesses one charge of positive electricity and each chloride ion one charge of negative electricity. A sodium hydroxide molecule breaks up into a positively charged sodium ion and a negatively charged hydroxide ion. Ions of opposite electrical charge cannot

be separated from each other under any ordinary conditions because of the powerful attraction of opposite electrical charges for each other. This makes it impossible to stock and use alone either hydroxide ions or hydrogen ions. We do not alter pH values by adding either ion alone, but by adding some material that furnishes one or the other kind of ion when dissolved in water.

"Hydrogen ion and hydroxide ion unite chemically to form neutral water. Thus $H^++OH^-=H_2O$. Water is really a compound of equivalent amounts of acid and alkali. However, it is dissociated into ions to an extremely small degree. This dissociation is represented by the equation $[H^+]\times[OH^-]=0.000,000,000,000,000,001$, where $[H^+]$ represents the number of grams of hydrogen ion in a liter and $[OH^-]$ represents the equivalent number of hydroxide ions. (A hydroxide ion weighs 17 times as much as a hydrogen ion.) Thus the number of free ions in pure water is relatively very minute.

"If we increase $[H^+]$ one hundredfold by adding acid, we decrease $[OH^-]$ to 1 per cent of its value. If we know the value of $[H^+]$ in any solution, we can calculate the value of $[OH^-]$ from the above equation. Thus, in order to calculate either the active acidity or the active alkalinity of any solution, we have only to measure the value of $[H^+]$, which can be done either with the glass electrode or by means of standard solutions of indicator dyes.

"A tenth-normal solution of hydrochloric acid contains 0.0948 gram of [H⁺] per liter. A tenth-normal solution of sodium hydroxide contains 0.000,000,000,000,000,01/0.0929 or 0.000,000,000,108 gram of [H⁺] per liter. It is awkward to use such tiny numbers and a range so great as that to be found in ordinary tannery liquors. Scientific men are usually mathematicians and find it much easier to use the logarithms of these numbers instead of the numbers themselves. The logarithm of 0.0948 is -1.02; the logarithm of 0.000,000,000,000,108 is -12.97. Since practically all solutions used in practice have negative values for the logarithm, it is convenient to drop the minus sign in front of the logarithm. The number then becomes what has been defined as the pH value of the solution. The "p" stands for pressure or activity and the "H" for hydrogen ion. We may then define pH value as $-\log$ [H⁺].

From this we construct the pH scale. In pure water, $[H^+] = [OH^-]$, or $[H^+] = 0\,000,000,1$. Log $[H^+] = -7.0$. The neutral point on the scale is thus taken as 7. When the pH value is higher than 7, the solution is alkaline; when lower than 7, it is acid. In making thermometers, some arbitrary value is taken as zero; temperatures above this point are denoted by plus signs and lower temperatures by minus signs. It would probably have suited the tanner better to have taken the neutral point of a solution as pH = 0, denoting increasing acidity by plus signs and increasing alkalinity by minus signs. He would then have been able to call the pH value of a tenth-normal solution of hydrogen ion +6 and the pH value of a tenth-normal solution of hydroxide ion -6, indicating the absolute value of the number increasing with increasing acidity, with plus signs, and the number increasing with increasing alkalinity, with minus signs. However, the present pH scale is so universally used that the tanner may as well accept it, even though increasing acidity is indicated by decreasing pH value.

"A solution containing one gram of hydrogen ion per liter has a pH value of zero; 0.1 gram per liter a pH value of 1; 0.01 gram per liter a pH value of 2; 0.001 gram per liter a pH value of 3; 0.000, 1 gram per liter a pH value of 4; 0.000,01 gram per liter a pH value of 5; 0.000,001 gram per liter a pH value of 6; and pure water, which contains 0.000,000, 1 gram of hydrogen ion per liter a pH value of 7.

"A hydroxide ion weighs 17 times as much as a hydrogen ion and so pure water contains 0.000,000,1 gram of hydrogen ion and 0.000,001,7 gram of hydroxide ion per liter. A solution containing 0.000,017 gram hydroxide ion per liter has a pH value of 8; 0.000,17 gram per liter a pH value of 9; 0.001,7 gram per liter a pH value of 10; 0.017 gram per liter a pH value of 11; 0.17 gram per liter a pH value of 12; 1.7 gram per liter a pH value of 13; and a solution containing 17 grams hydroxide ion per liter a pH value of 14. Thus the entire range of pH values found in the tannery are covered by a range of numbers from 0 to 14.

"A drop in pH value of 1.0 means that the amount of hydrogen ion has been increased tenfold; a drop of 2.0 that it has been increased one hundredfold; a drop of 3.0 that it has been increased one thousandfold, etc. A rise in pH value of 1.0 means that the concentration of hydroxide ion has been increased tenfold; a rise of 2.0 one hundredfold; a rise of 3.0 one thousandfold, etc."

Origin of Name

Many tanners express curiosity as to how the name pH was derived. In the quantitative development of theories of physics and chemistry, it had become customary to represent the *pressure* or *activity* exerted by molecules or ions in a given system by a small p (for pressure) placed before the chemical symbol for the molecule or ion. The symbol for hydrogen is H, and so the activity of the hydrogen ion was represented by pH.

Colorimetric Measurement of pH Value

The original measurements of pH value were made with what is known as a hydrogen electrode; but, based upon hydrogen-electrode measurements, many new and much easier methods have been developed. For most tannery liquors, an electrometric method is now used, employing what is known as the glass electrode. For soak waters and bate liquors, it is much easier and quicker to use the colorimetric method, in which certain dyes are used which change color with changing pH value.

The colorimetric method will be described for the LaMotte Block Comparator. The dye indicators used, the pH ranges covered by each and the color changes are listed in Table 21.

Table 21. Dye Indicators and pH Ranges of Color Changes.

Indicator	pH Range	Color Change
Acid Cresol Red	0.2- 1.8	Red-Yellow
Meta Cresol Purple	1.2- 2.8	Red-Yellow
LaMotte Yellow	2.6- 4.2	Red-Yellow
*Alpha (2:4) Dinitrophenol	2.8- 4.4	Colorless-Deep Yellow
Bromphenol Blue	3.0- 4.6	Yellow-Blue
Bromcresol Green	3.8- 5.4	Yellow-Blue
*Gamma (2:5) Dinitrophenol	4.2- 5.8	Colorless-Deep Yellow
Methyl Red	4.4- 6.0	Red-Yellow
Chlorphenol Red	5.2- 6.8	Yellow-Red
*Para Nitrophenol	5.4- 7.0	Colorless-Deep Yellow
Bromthymol Blue	6.0- 7.6	Yellow-Blue
Phenol Red	6.8- 8.4	Yellow-Red
Cresol Red	7.2- 8.8	Yellow-Red
*Meta Nitrophenol	7.2 - 8.8	Colorless-Deep Yellow
Thymol Blue	8.0- 9.6	Yellow-Blue
LaMotte Oleo Red B	8.6-10.2	Yellow-Red
LaMotte Purple	9.6-11.2	Purple-Red
LaMotte Sulfo Orange	11.0–12.6	Pale Yellow-Deep Orange
LaMotte Violet	12.0-13.6	Red-Blue

^{*} These indicators are for special work.

For many years before the tanner had ever heard of the concept of pH value, he used litmus to determine whether a liquid was acid or alkaline. For pH values below 6.2, litmus turns red in color, indicating the presence of acid; for pH values above 8.0, litmus turns blue in color, indicating the presence of alkali. Between the pH values of 6.2 and 8.0, litmus is actually unreliable as an indicator and so is not used in modern practice.

The indicators listed in Table 21 are all very reliable over the ranges of pH value given; at pH values below the range, the indicator has the color shown to the left and at higher pH values, the color shown to the right. For example, below 6.0, Bromthymol Blue has a yellow color, but above 7.6, it has a blue color. Between 6.0 and 7.6, it is a mixture of yellow and blue, or green. As the pH value

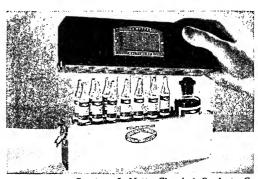
is raised gradually from 6.0 to 7.6, it changes quite gradually in color from yellow, through various shades of green to blue. By comparing the color with a standard, the pH value between 6.0 and 7.6 can be determined with an accuracy of 0.1. Each indicator covers only the pH range indicated. By selecting a sufficient number of indicators, the tanner can cover the range from 0.2 to 13.6, which is a far wider change than is ever found in a tannery.

Until a tanner becomes familiar with the pH ranges of his liquors, he must try one indicator after another until he finds the one that covers the range, but this can be done very systematically. Suppose, for example, that he had a liquor with a pH value of 4.7, but not knowing what it was, he used Bromthymol Blue. It would turn yellow, indicating a pH value of 6.0 or lower. He would then make a test with Chlorphenol Red and it would turn yellow, indicating a pH value of 5.2 or lower. He would then make a test with Methyl Red and it would turn to a red-to-orange color, and he would find it to match the Methyl-Red standard color for a pH value of 4.7.

A typical LaMotte Comparator is shown in Fig. 110 with its cover being removed. Both cover and base are slotted to hold 14 small vials or tubes and a bottle of the indicator equipped with a pipette marked to deliver a volume of exactly 0.5 cubic centimeter. There is a separate Comparator for each indicator. For Bromthymol Blue, there are 10 hermetically sealed tubes, one of which con-

Fig. 110.

LaMotte Block Comparator



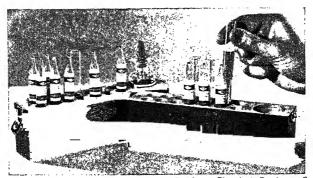
Courtesy LaMotte Chemical Products Co.

tains distilled water and the other 9 solutions of the indicator at pH values of 6.0, 6.2, 6.4, 6.6, 6.8, 7.0, 7.2, 7.4 and 7.6, respectively, thus showing a range of colors from yellow, through a range of greens to blue. There are also 3 empty, open tubes, each with a mark indicating a volume of 10 cc.

When the cover is removed, it is placed on the table upside down as shown in Fig. 111. It is equipped with a frosted-glass window on one side and 3 slots on the other so that the colors of three pairs of tubes can be compared at one time. The tubes are used in pairs, because many liquors are turbid and it is necessary to have the same degree of turbidity for all samples being matched.

In order to make a measurement of pH value of a liquor, fill the 3 tubes with the liquor, to the 10 cc. mark, but into only one of them pipette 0.5 cc. of the indicator. Place them in a row in the 3 windowed slots, with the one containing indicator in the middle and in front of it, in the next row, place the sealed tube of distilled water. In the other two slots in the front row, place two of the color standards differing in pH by only 0.2, as, for example, the tubes marked 6.8 and 7.0. Look through the three pairs of tubes, holding them toward a window or any other

source of daylight, and change the color standards, if necessary, until the middle pair of tubes either exactly matches in color one of the other pairs or lies between them in color. If an exact match is obtained, the pH value is read directly from the standard tube. If the color lies between those of the pairs on either side, the pH value is taken as the average of the two standards.



Courtesy LaMotte Chemical Products Co.

Fig. 111. Comparator Set Up for Use.

If the match is made with the standard of lowest or highest pH value in the set, the measurement should be repeated with the next indicator in pH range. No pH value should be accepted as final unless it lies between the extremes of the standards for any given indicator. Usually a test can be completed in a fraction of a minute. The electrometric measurement of pH value is described in Chapter 10.

Soaking Dry Goatskins

Of the more than 39 million goatskins tanned in the United States annually, about 97 percent arrive at the tanneries in the dried condition. Dried stock is very much more difficult to soak back properly than green, salted stock, and the problem is greatly complicated for goatskins because of the fact that the methods employed in drying them differ greatly in different parts of the world. Those that are first cured properly with reasonably pure salt and then dried present very little difficulty and can be soaked back satisfactorily in water alone. Those that are flint dried often require the aid of materials like caustic soda to aid them in absorbing water. Some skins are first treated with very impure salts containing alum and other materials that act as mild tanning agents, and then dried; they often cause very great difficulties in soaking and, later on, in unhairing.

In order to be soaked properly, a dried goatskin should take up about 200 percent of its dry weight of water; that is, a 1-lb. skin should increase in weight to about 3 lbs. by absorbing water. In practice, this is rarely, if ever, attained. If a flint-dried Amritsar skin is soaked for 3 days in 15 lbs. water per lb. of dry skin at 52 °F., it will absorb only about 30 percent of its weight of water; but under the same conditions a dry, salted China skin may absorb 120 percent of its weight of water. If we soak each skin in pure water for 1 day, then for 1 day in water containing 1 lb. caustic soda per 100 lbs. dry skin, and then for 1 day in pure water, the Amritsar skin about 170 percent. A Bagdad skin will absorb an amount intermediate

between the two.

If an excessive amount of caustic soda or other alkali is added to the soak water, the stock swells excessively against a resistance caused by the blood-vessel structure of the skin, and permanent strains are produced that persist even in the finished leather as an unsightly "wild grain."

Because of the difficulty with which dried stock takes up water, most goatskin tanners assist the takeup by milling the stock in a revolving drum between successive soakings. This causes a flexing of the stock which helps to separate fibers glued together and greatly facilitates the absorption of water.

The simple procedure given above for green, salted calfskins can be used successfully by any tanner, although many tanners prefer to vary it by using warmer water for a shorter soaking time or with antiseptics; but no such simple procedure can be laid down for goatskins because of their wide variations in condition. However, the following procedure will serve any tanner of dry goatskins as a first approximation, and he can readily learn by practice how to vary it for his different classes of stock.

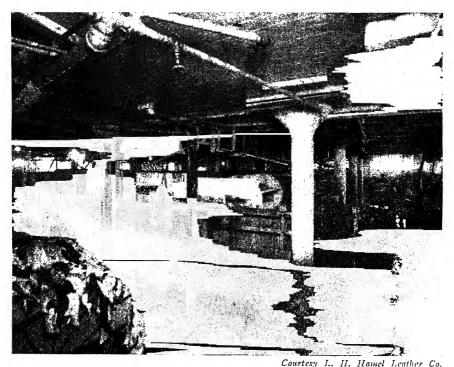
Into a 2500-gal. vat filled with clean water at 52 °F. put 1600 lbs. of dry goatskins, one by one, and let them remain there for 24 hours. Then haul out the pack and run the water to the sewer. Put the pack into a revolving drum and wheel for 10 minutes to "break" the stock. Continue to run the drum while flushing the stock with a good supply of running water for 10 minutes, and then dump the pack. Refill the vat with clean water at 52 °F., add 16 lbs. of caustic soda and mix thoroughly. Put the skins back into the vat one by one and allow them to remain there for 24 hours. Then haul out the stock, run the used liquor to the sewer, refill the vat with fresh water alone at 52 °F. and put the skins back into it one by one, allowing them to remain there for another 24 hours. Then haul them out and send them on for the unhairing operations.

For vats of other sizes, simply use the same ratio of stock to water as that given above. For various types of stock, tests should be made increasing or decreasing the amount of caustic soda used and increasing the time of soaking, taking care to replace the used water by fresh water every day. By putting a paddle wheel in the vat, the water can be changed satisfactorily without hauling out the stock. Before draining off the water, run the paddle for 2 minutes and then drain, refill, run the paddle 2 minutes and let stand. This is good practice either when extending the time of soaking or when speeding up the soaking by using warmer water. The frequent changing of the water is a safeguard against bacterial damage.

Some tanners prefer not to use caustic soda, because of the danger of getting an excessive quantity into the stock, and soak for one day in water containing 80 lbs. common salt per 100 gals. and then for two days in changes of pure water to remove the salt. Others use mild alkalies, such as borax or soda ash. The use of alkalies not only speeds up the absorption of water by the stock, but it also inhibits bacterial action, which is greatest in tannery soak waters at pH values between 6.5 and 8.0. When using alkalies, pH tests of the soak waters should be made at intervals; the amounts of alkali used should be such as to keep the pH value below 11 after the stock and alkali have been in contact for an hour or more. Some tanners do not soak their stock sufficiently, but rely upon the action of the lime liquors used later to complete the soaking action. However, all the writer's experiences with all kinds of raw stock indicate that finer leather is always produced by soaking the stock fully and well before allowing it to go to the lime liquors. Tanners should always be on the alert to use antiseptics in the soak waters whenever conditions are such as to produce the slightest fouling of the liquors.

Fig. 112 shows a department in a goatskin tannery where goatskins are both soaked and limed in the same vats equipped with paddle wheels. Down the aisle to the right, in the background, a man can be seen pushing a truck of dry goatskins to the soaking vats. On the left of the aisle, a man can be seen hauling soaked skins out of a vat. At the left of the picture can be seen a truckload of skins ready for milling after soaking one day.

As a rule, goatskins are not fleshed until after they have been unhaired. The general rules for soaking dry goatskins apply equally well to kangaroo skins and many other types of light, dry skins.



Courtes, 1., 11. Hamel Leanner C.

Fig. 112. Soaking Department in a Goatskin Tannery.

Soaking Green, Salted Heavy Hides

Reasoning logically, heavy hides should be soaked for a longer period of time than calfskins, but many sole-leather tanners limit the soaking of heavy steer hides to one day because of the fear that bacterial action may occur in the middle of the hides and cause a depletion that will prevent the making of firm and solid sole leather. Heavy hides that have not been well cured may be infected with bacteria throughout their entire thicknesses. Antiseptics do not penetrate heavy hides very rapidly, and bacteria deeply seated in a hide begin to multiply just as soon as enough salt has been leached out in the first stages of soaking. Improperly cured stock is a hazard at best, and it should be rushed through the soak vats and into the lime liquors as quickly as it can be done reasonably satisfactorily, flushing the stock with

running water in a revolving drum, cold water and antiseptics. Sometimes it is desirable to soak such stock only for 1 day in strong salt brine and then wash to remove the salt.

If the facilities are available and it is desired to make sole or other heavy leather from choice, big-packer stock to be made into leather of highest quality, the writer recommends the following procedure. Upon receipt of the stock at the tannery, open the bundles and lay the hides out flat in small piles in cold storage, turning them over frequently to permit uniform and complete chilling. After they have been in cold storage for at least a week, put about 1000 lbs. at a time into a drum about 8 ft. in diameter and 5 ft. wide and geared to run with this load at 12 revolutions per minute. The rounded pegs within the drum should not extend outward more than 6 inches. Fill the drum to the gudgeon with water at 52 °F. and run 3 minutes. Then put on the slatted door instead of the tight door, start the drum running and pass running water through the hollow gudgeon at a rate of not less than 100 gals. per minute. The temperature of this water should be about 52 °F. and washing should be continued for 15 minutes with the drum running. Then the stock should be taken out for soaking.

Fill a clean 2500-gal. vat with fresh water at 52 °F. and lay 5000 lbs. of washed hides into it one by one and leave them there for 24 hours. Then flesh the stock carefully and put it back into a fresh soak water made up exactly like the first. Every day, haul out the stock, run the used water to the sewer and make up with fresh water at 52 °F. and put the stock back. Repeat this until the stock has been soaked for 5 days. When water warmer than 52 °F. must be used, the soaking period must be shortened accordingly. Then haul it out and send it to the lime liquors. Compared to the old-fashioned 1-day soak, this procedure produces finer leather of greater gains in appreciably less time in the subsequent tan liquors.

Soaking Dry, Heavy Hides

The proper soaking of dry hides is difficult only when it is of poor or varying quality. The following procedure will be found satisfactory for most dry hides. Fill a 2500-gal. vat with fresh water at 70 °F. and add 200 lbs. of salt, 8 lbs. of caustic soda and 1 lb. of chlorine. Mix well and put 1500 lbs. of dry hides into it one by one and allow them to remain there for 24 hours. Many dry hides arrive at the tannery folded over once along the backbone line. These go into the soak vat without attempting to unfold them. After soaking for 24 hours, haul out the stock and run the liquor to the sewer. Refill the vat with fresh water at 70 °F. and add 200 lbs. of salt, 4 lbs. of caustic soda and 1 lb. of chlorine and mix well. Unfold the hides so that they will lie as flat as possible and put them into this second soak liquor, one by one. After the stock has been in the second soak water for 24 hours, haul it out, run the liquor to the sewer and make up a third soak water exactly like the second and put the stock back into it for another period of 24 hours. Then haul out the stock and divide it into 3 equal parts. Put each part into a drum, like the one described above for packer hides, and run for 1 hour without adding any water. Then wash with a good flow of running water for 25 minutes. When all 3 parts have been washed, put them together again as a single pack. Make up a fourth soak water exactly like the third and put the stock back to soak for another period of 24 hours. Then haul out the stock and flesh it on the fleshing machine. If it still feels unduly firm and wiry, put it back into the drum and run it without water for from 5 to 30 minutes, depending upon the firmness. Then put the stock back into the soak vat with fresh water only at 52 °F. Haul it out daily and make up a fresh soak with water only at 52 °F. Continue this until the pack has been soaked a total of 7 days or longer, if necessary to get it fully soaked. It is then ready to go to the lime liquors for unhairing.

McLaughlin has successfully soaked all kinds of dry stock without the use of alkalies by soaking them first in solutions of from 80 to 160 lbs. of common salt per 100 gals. water for from one to two days followed by successive changes of fresh water to remove the salt and allow the stock to take up enough water. The same salt solutions can be used for several lots of stock. The salt greatly retards bacterial action and assists in the absorption of water by the stock.

In all soaking operations, it would be well to keep in mind Figs. 95 to 98 (p. 177-8). During partial drying, the fibers become distorted and must be made to reabsorb their normal contents of water in order to bring them back to their normal sizes and shapes. It is also very important that they be freed as far as possible from blood and soluble proteins before they are put into the lime liquors. These materials not only tend to pollute the lime liquors, but must be removed at some stage before the tanning, or poor leather will result. When the soluble proteins dry, they act as a cement, gluing the fibers together and tending to make flat and hard leather.

Excessive drumming and mechanical action should always be avoided because they may cause the production of loose and grainy leather.

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Chapter 8

Unhairing

All the departments of the tannery in which the hides and skins, after leaving the hide house, are washed, soaked, fleshed, unhaired, bated and prepared for the initial tanning operations are known collectively as the *beamhouse*. It is an old name derived from the wooden beams, like those shown in Fig. 94, of Chapter 7, over which hides and skins were thrown to be trimmed, unhaired and scudded by hand. Actually, the washing, soaking and fleshing operations described in Chapter 7 belong to the beamhouse operations, as do also the deliming and bating operations to be described in Chapter 9.

The primary object of the beamhouse operations is to rid the hides and skins of those portions that are not desired in the finished leather and to put them in proper chemical and physical condition for the subsequent processes. In order to make good leather, this must be done in such manner that no damage is done to the fibrous portion used in making leather nor to its natural structure, and the stock must be put in optimum condition for the tanning operations that follow. In the soaking department, the stock is trimmed, fleshed, freed from blood, dirt and water-soluble materials and restored to a natural condition by absorbing water.

For making most leathers, the hides and skins must be freed from hair and epidermis and from the glands of the thermostat layer. These structures are made up of proteins of the class known as *keratin*. The fibrous portions to be converted into leather are made up of the class of proteins known as *collagen*. In trying to separate the keratin from the collagen without damage to the collagen, it is important to recognize the differences in properties between these two kinds of protein. Both keratin and collagen can be destroyed by strong solutions of acids or alkalies, but acids destroy collagen more readily than they do keratin and alkalies destroy keratin more readily than they do collagen. For this reason, the separation is usually effected in alkaline solutions.

If a calfskin is immersed in a solution containing 1 lb. of caustic soda per gallon of water, the hair will be quickly dissolved, but the true skin will not be irreparably damaged until long after all the hair is gone. The writer has unhaired calfskins in this manner and made fair leather, but the method is a dangerous one because strong alkali will destroy the collagen in the course of time. The pH value of such a solution is about 14.0. At this pH value, collagen becomes hydrolyzed or destroyed in the course of time, although hair and epidermis are quickly destroyed.

Centuries ago, tanners discovered that a solution of lime can be used safely to separate hair from skin with relatively little damage to the skin. The reason for this is that lime has a limited solubility. If 1 lb. of lime (calcium hydroxide) is put into a gallon of water, from 99.4 to 98.5 percent of it will remain undissolved, because the solution becomes saturated at about 0.006 lb. per gal. in water at the boiling point and at about 0.015 lb. per gal. in water near the freezing point. A saturated solution of lime at 70 °F. has a pH value of about 12.5. It cannot be raised above this point by adding more lime because the excess will not dissolve.

Microscopic Study of Action of Limewater on Calfskin

Because saturated limewater is so universally used in unhairing hides and skins it is of very great practical importance that the tanner be as familiar as possible with the action of limewater on raw stock.

Wilson and Daub made a study, under the microscope, of the structure of calf skin during 7 months' contact with saturated limewater. They cut the butt of a fresh calf skin into pieces 12×36 millimeters, soaked them in water at 44.6° F. for 1 day, and then put them all into a closed jar containing 1 liter of water and 27 grams of calcium hydroxide, an amount sufficient to keep the solution saturated at all times. The jar was kept in an incubator at 68° F. and pieces were drawn from it periodically. These were prepared for examination under the microscope by washing, dehydrating, imbedding, sectioning both vertically and horizontally, staining, mounting, and photographing. A second series was run in which the limewater was covered with a layer of toluene. Both series gave exactly the same results and both proved to be sterile, at least for 6 months. After 7 months the liquor without toluene showed a count of 1 per cc.; only a



Fig. 113. Horizontal Section of Calf Skin through Sebaceous Glands. (after soaking, before liming)

Location: butt.

Thickness of section: 30 microns, or 0.00118 inch.

Magnification: 190 diameters.

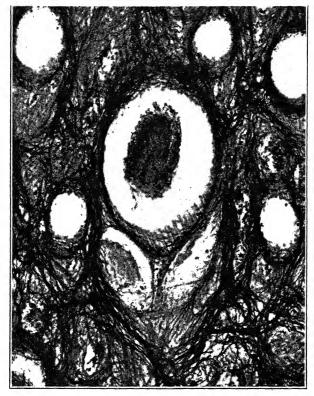


Fig. 114. Horizontal Section of Calf Skin through Sebaceous Glands. (after 3 weeks' contact with sterile limewater).

Location: butt.

Thickness of section: 30 microns, or 0.00118 inch.

Magnification: 190 diameters.

single colony developed from 1 cc. on agar during 4 days' incubation. We may thus infer that the changes occurring in the skin during the long contact with limewater were not caused by bacteria.

The first action noticeable was a slow disintegration of the cells of the Malpighian layer of the epidermis. By the end of 5 days this action had proceeded far enough to permit the easy removal of hair and epidermis by scraping with a blunt knife. Little further change was noticeable until after the third week.

For purposes of illustration, it was found best to use horizontal sections cut through the sebaceous glands. These were stained with Van Heurck's logwood and Daub's Bismarck brown. Fig. 113 shows a section of the fresh skin after soaking in cold water for 1 day. In the center is a cross-section of a hair running nearly at right angles to the plane of the page. Just below it, to the left and right, is a pair of sebaceous glands, which furnish oil to the hair follicle. Surrounding both hair and glands are thin strands of elastic fibers. The dots are the stained nuclei of epithelial cells.

Fig. 114 shows a similar cutting of the skin 3 weeks after being placed in

the limewater. The glands have been attacked, and nearly all the epidermal cells surrounding the hair have disappeared, leaving it resting loosely in the empty follicle.

The elastin fibers still show up sharply after 3 weeks, but begin to break down rapidly about the fourth week. In Fig. 115 the remnants of elastin fibers appear blurred. At the end of the fifth week the elastin fibers have entirely disappeared, as shown in Fig. 116.



Fig. 115. Horizontal Section of Calf Skin through Sebaceous Glands. (after 4 weeks' contact with sterile limewater).

Location: butt.

Thickness of section: 30 microns, or 0.00118 inch.

Magnification: 190 diameters.

Many cell nuclei are still to be seen after 5 weeks, but are gradually destroyed and none are to be found after 3 months. The corneous layer of the epidermis and the hair appeared quite resistant to the action of lime for 15 weeks, but began to disintegrate slowly after this time, and had disappeared at the end of 7 months.

The collagen fibers, or leather-forming portion of the skin, remained sharply defined for 5 months, after which they assumed a blurred and glassy appearance and were slowly being hydrolyzed. After 7 months the skin had apparently lost

its power to become fallen, or flaccid, when placed in neutral ammonium chloride solution. Pickling with sulfuric acid and salt caused it to shrink to a hard mass, resembling a dehydrated plate of gelatin. When tanned, it yielded a very thin and empty leather, indicating a very heavy loss of collagen during liming.

Although there is a great difference in degree, saturated limewater actually hydrolyzes both keratin and collagen. The tanner should become familiar with the scientific term hydrolysis. It means "the chemical decomposition of a sub-

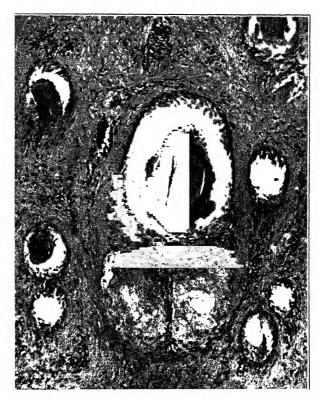


Fig. 116. Horizontal Section of Calf Skin through Sebaceous Glands. (after 5 weeks' contact with sterile limewater).

Location: butt.

Thickness of section: 30 microns, or 0.00118 inch.

Magnification: 190 diameters.

stance that occurs when water is absorbed by it, causing the formation of new substances." When proteins are hydrolyzed, they react chemically with water and break down into other substances, many of which are soluble in water.

Effect of Time and Temperature on the Hydrolysis of Skin and Hair by Saturated Limewater

In order to get more quantitative data on the hydrolysis of skin and hair by saturated limewater, Merrill and Fleming prepared some purified calfskin, free from hair and some purified calf hair, free from the true skin. One gram

portions of dry skin or hair were digested with 100 cc portions of limewater containing an excess of undissolved lime for the periods of time and at the temperatures shown in Figs. 117, 118 and 119. In most laboratory research the centigrade thermometer is used instead of the Fahrenheit thermometer commonly used in the tannery. The equivalence in degrees is as follows:

° C.	• F.
5	41.0
10	50.0
15	59.0
20	68.0
25	<i>77</i> .0
30	86.0
35	95.0
40	104.0

In order to convert ° C. into ° F., simply multiply by 1.8 and add 32.0.

At the end of the digestion period, each liquor was filtered and analyzed for its nitrogen content, from which the amount of protein dissolved was calculated.

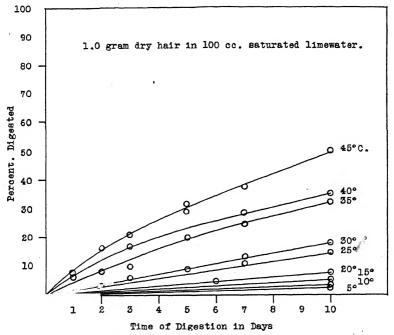


Fig. 117. How the Hydrolysis of Hair by Saturated Limewater Increases with Both Time and Temperature.

Fig. 117 shows that hair is continuously digested (dissolved) by limewater with time, but the rate of digestion is increased by increasing temperature. Fig. 118 shows that the same is true for the skin, but a startling increase in digestion takes place when the temperature is increased above 86° F. Fig. 119 shows that hair is more rapidly digested than skin up to 95° F., but that skin is digested

much more rapidly than hair at temperatures above 95° F. The information provided by Fig. 119 is of utmost importance to the practical tanner, but he must be cautioned against assuming that safety lies only in liming at low temperatures. If lower temperatures are used, the time of liming to get easy unhairing is increased, and a low temperature may result in more harm than a higher one carefully controlled.

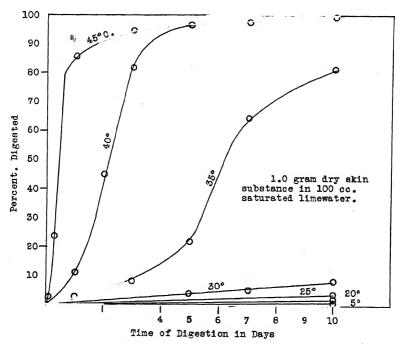


Fig. 118. How the Hydrolysis of Calfskin by Saturated Limewater Increases with Both Time and Temperature.

Sulfides

Long ago tanners discovered that the time required to get easy unhairing during liming is greatly shortened by adding sodium sulfide to the lime liquors. When sodium sulfide is dissolved in water, it hydrolyzes. Each molecule of sodium sulfide reacts chemically with one molecule of water, forming one molecule of sodium hydrosulfide and one molecule of caustic soda (sodium hydroxide).

Sodium hydrosulfide has a specific action on keratin. It reacts chemically with it, producing a modified form of keratin that is much more rapidly destroyed by alkali than the original keratin. On the other hand, sodium hydrosulfide appears to have no such action on collagen, and so provides an excellent means for making a more quantitative separation of keratin from collagen without causing any damage to the collagen.

Caustic soda reacts chemically with both keratin and collagen. When added to lime liquors, it causes inordinate swelling of skins and strains along the pattern of the blood-vessel system that result in grainy leather and drawn flanks. Until recently, pure sodium hydrosulfide was not commercially available to tan-

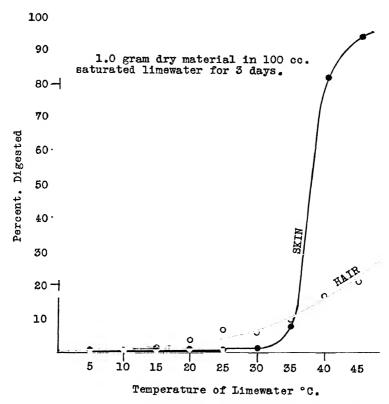


Fig. 119. How the Hydrolysis of Both Skin and Hair by Saturated Limewater Increases with Temperature During a 3-Day Liming Period.

ners, and so they used ordinary sodium sulfide, usually in the form of a fused product containing 60 percent by weight of sodium sulfide and 40 percent of water. When 100 lbs. of this 60 percent sodium sulfide is dissolved in water, it immediately reacts chemically with 14 lbs. of water, forming 43 lbs. of sodium hydrosulfide and 31 lbs. of caustic soda. Because of the damaging effects of the caustic soda, tanners had to limit rather sharply the amounts used, often to the point where they were not taking full advantage of the sodium hydrosulfide.

Fortunately, pure sodium hydrosulfide has now become available commercially to tanners and at a cost no greater than that of the old sodium sulfide. It is available in liquid form, containing 38 percent sodium hydrosulfide and 66 percent water (in steel drums), and also in solid form containing about 70 percent sodium hydrosulfide by weight. Contact of sodium hydrosulfide with air must be avoided as far as possible before actual use because it readily combines chemically with oxygen, forming products which have little or no unhairing action and which form caustic soda when mixed with limewater. The liquid product has the disadvantage of a higher freight rate per unit of sodium hydrosulfide, but it has the great advantage of simplicity of handling and preventing undue contact with air; the solid product must be dissolved before using and sometimes cakes in the drum.

At the time of this writing, developments are in progress in the commercial production of calcium hydrosulfide which cannot form any caustic soda when added to limewater. It can readily be produced in the laboratory by saturating limewater containing an excess of undissolved lime with hydrogen sulfide gas. On a large scale in the tannery, it is a disagreeable operation and hardly practical for the average tanner. However, by the time this book is published, or shortly thereafter, calcium hydrosulfide should be available commercially, and will become a great boon to many tanners.

Calcium hydrosulfide has the same activity on keratin as sodium hydrosulfide, but, when added to lime liquors, it decreases the solubility of the lime and produces pH values well below 12.5 of pure, saturated limewater. In making fine, smooth leather, it is necessary to prevent undue swelling and plumping of the raw stock. When calcium hydrosulfide is added to lime liquors, less swelling takes place than when pure limewater is used, and a smoother leather results. The writer has used calcium hydrosulfide on calfskins in quantity sufficient to dissolve the hair completely and has produced beautifully smooth leather of the very highest quality.

Liming and Unhairing Green, Salted Calfskins

In making any specific type of leather, all operations employed are interrelated. A change in any one operation often necessitates compensating changes in others. The best procedure to follow in a given operation depends upon the

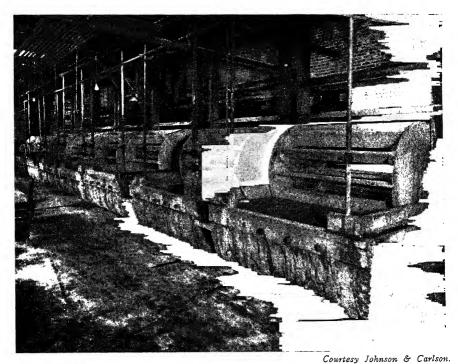
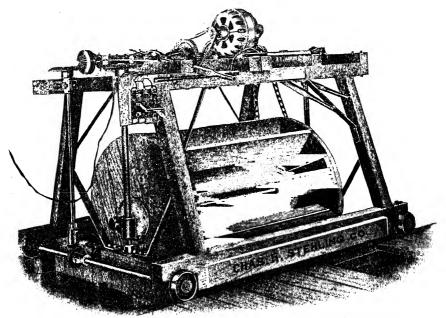


Fig. 120. Battery of Paddle Vats Used for Liming Skins.

details of operations which precede and follow it. The following procedure for liming and unhairing calfskins is the one the writer has found best for calfskins soaked and fleshed according to the procedure given in Chapter 7. It is for a pack of 500 calfskins weighing 5000 lbs. after soaking. If the average weight of the skins is greater, they usually contain a lesser percentage of water; the quantities of materials used per unit total weight of the pack should therefore be increased for greater average weight per skin and decreased for lesser average weight.

The writer prefers liming in vats equipped with paddle wheels, although some tanners use only still vats in order to avoid mechanical action that may make the leather loose and grainy. The object of the paddle wheel is to stir up the undis-



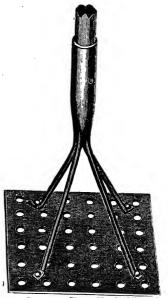
Courtesy Chas, II. Stehling Co.

Fig. 121. A Portable Paddle Wheel.

solved lime occasionally to keep the solution saturated, to assist the diffusion of the lime between and into the skins and to prevent the skins from packing. If it is run no more than is necessary to do this, excellent results can be obtained. For a 5000-lb. pack, a paddle vat is used having a total capacity of 2500 gals. A battery of 7 paddle vats is shown in Fig. 120. Sometimes one portable paddle set on a track is used for a whole row of vats. Such a portable paddle is shown in Fig. 121. Each vat is equipped with a device for heating the liquor. This may be done by pumping the liquor through heating coils or by running live steam directly into the liquor, in which case a slotted wooden covering, known as a steam box, is placed over the steam outlet to protect the stock from direct contact with the steam. The paddle wheel is run at about 20 revolutions per minute. Where still vats are used, the stock is hauled out occasionally and the

liquor plunged by hand with a plunger like that shown in Fig. 122 attached to a long pole.

Fill the vat with water to the 1900-gal. mark, add 150 lbs. of hydrated lime and 25 lbs. of liquid sodium hydrosulfide. Start the paddle wheel running and put the 5000 lbs. of stock into the liquor. With the paddle running, apply heat until the temperature of the liquor reaches 82° F. Then stop the paddle wheel and let the stock remain still for 6 hours. Then run the paddle wheel for two minutes while applying heat, to bring the temperature of the liquor back to 82° F., if it has dropped below this point. Repeat this at the end of the 12th hour and again at the end of the 18th hour. When the stock has been in the liquor for 24 hours, it should be ready for unhairing, but, if the hair should not then slip easily, the stock must be left in the liquor until it does. The stock should not be



Hand Plunger Used for Mixing and Agitating Lime Liquors.

Fig. 122.

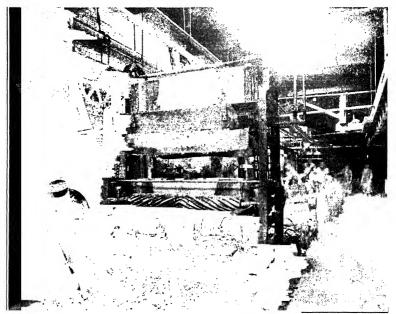
Courtesy Chas. H. Stehling Co.

left in the liquor longer than is necessary to get easy unhairing, and excessive running of the paddle wheel should be avoided. If successive packs show difficulty in unhairing at the end of 24 hours at 82° F., increase the percentage of sodium hydrosulfide used. Some tanners lime for a longer time at lower temperature, but whatever temperature is used, it is extremely important to maintain it accurately.

When the hair slips easily, haul out the pack and unhair the skins on an unhairing machine, of which there are several types. In principle, the unhairing machine is like the fleshing machine, but the blades are not sharpened to cut away any portion of the skin, but merely to rub the hair off the grain surface of the skin without scratching or causing any damage to the grain. Fig. 123 shows one type of unhairing machine operating like a Ferris wheel. A skin is thrown over one of the rubber bolsters in the series and it is drawn mechanically up between two revolving cylinders equipped with spiral blades which press the

skin against the rubber bolster and brush off the hair. After one complete revolution, the position of the skin on the bolster is shifted so that, on the second time through, the blades will cover the narrow strip along the top edge of the bolster not unhaired the first time through. Upon coming through the second time, each skin is thrown on to a pile to be scudded later.

Fig. 124 shows a cross-section of calfskin taken from a lime liquor run according to the foregoing procedure, except for the fact that a smaller amount of ordinary sodium sulfide was used and the stock was left in the liquor for two days. (Sodium hydrosulfide was not commercially available at the time). The swelling action of the lime has caused the skin to become plump and rubbery in



Courtesy A. F. Gallun & Sons Corp.

Fig. 123. One Type of Machine Used for Unhairing Calfskins.

feel. The hydrolyzing action of the lime and hydrosulfide has extended only to the cells of the Malpighian layer of the epidermis, which is the layer of youngest cells adjoining the true skin. The hair and the corneous, or outer layer, of the epidermis remain intact. However, the destruction of the Malpighian layer effects a complete severing of the true skin from the hair and the corneous layer of the epidermis, and these can be removed by simply rubbing or brushing them off in the unhairing machine. This section was stained before photographing with a dye that colors the elastin fibers a dark blue, and they appear in the thermostat layer and in the lowest level of the skin as dark areas.

They can be seen more clearly in Fig. 125, which shows the thermostat layer at much higher magnification. The lime and hydrosulfide have caused disintegration not only of the epidermis lining the hair follicles, but also of the sudoriferous glands (oil glands) and the sweat glands. Remnants of the epithelial tissues can be seen in the hair follicles.

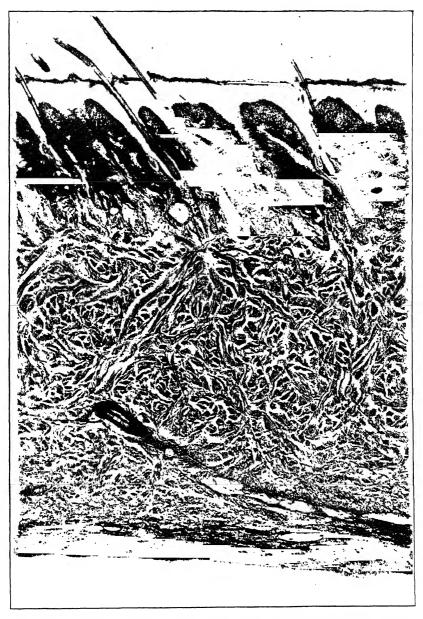


Fig. 124. Vertical Section of Calf Skin after 48 Hours in Lime Liquor.

Location: butt. Thickness of section: 40 microns, or 0.00158 inch. Magnification: 25 diameters.



Fig. 125. Thermostat Layer of Calf Skin after 48 Hours in Lime Liquor.

Location: butt.

Thickness of section: 40 microns, or 0.00158 inch. Magnification: 135 diameters.

Fig. 126 shows a workman hauling calfskins from a lime liquor in a paddle vat. Fig. 127 shows workmen hauling calfskins from a lime liquor in a still vat. The skins are being piled up on a truck to the left of the man working on the unhairing machine, which is of a type different from that shown in Fig. 123.



Fig. 126. Hauling Calf Skins from Lime Liquor in Paddle Vat.

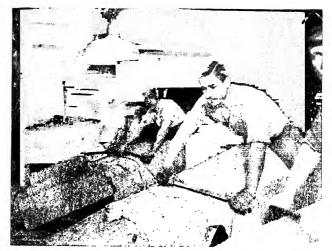


Courtesy B. D. Eisendrath Tanning Co.

Fig. 127. Hauling Calfskins from Lime Liquor in Still Vat and Unhairing on Machine.

This is more nearly like the fleshing machine. Each skin is first fed into the machine over half of its length and it is forced out toward the operator as it is being unhaired. When it has come out, the operator turns the skin around and then feeds the unhaired portion of the skin into the machine. After unhairing each skin, he throws it on the truck to his right to be sent for scudding.

Where still vats are used, it is necessary to pull the stock out at intervals and to plunge the liquors, that is, to agitate them with special plungers like that shown in Fig. 122, operated by hand, so as to stir up the undissolved lime and maintain saturation. With still vats, it is customary to put the same pack of skins through several vats, hauling them over from one vat to another and plunging each vat before a pack enters it. The same liquors are used for numbers of successive packs. Older liquors present some advantages over fresh ones: they contain dissolved protein matter that keeps the undissolved lime in suspension



Courtesy A. F. Gallun & Sons Corp.

Fig. 128. Scudding Calfskins on the Beam.

more effectively; they contain ammonia, and amines, resulting from protein decomposition, that assist in the unhairing action, and they contain calcium salts of weak organic acids that decrease the solubility of the lime, causing a lower pH value and less swelling of the stock. However, accumulating material dissolved from the stock makes uniform results more difficult.

The same advantage of the used lime liquor is obtained in the single liquor used in a paddle vat by running only one-half of the used liquor to the sewer after a pack has been limed and making up the other half with fresh lime liquor. Until a balanced system has been developed by practice, it is desirable to analyze each liquor after use and to add only enough lime and hydrosulfide to restore the concentrations to that indicated in the foregoing procedure.

Often the lime and hydrosulfide are mixed with water in a wooden tank and then run into the liming vats. A strong solution of sulfide or hydrosulfide is stored in an iron tank and any iron sulfide present is allowed to settle. The clear liquor is drawn off for use and mixed with the lime and water.

When only powdered, hydrated lime and liquid sodium hydrosulfide are used in a paddle vat, there is no need for premixing; they can be weighed off and dumped directly into the vat separately, with the paddle running.



Fig. 129. A Typical Beam Knife.

Scudding Calfskins

After the skins have been unhaired, the hair follicles still contain remnants of epithelial tissues, hair pigments and glands and lime soaps which must be removed before tanning. It is customary to do this by an operation known as scudding. This is frequently done by hand over a rounded wooden beam on which the workman usually first builds up a foundation of several skins. Fig. 128 shows a beamster in the act of scudding a calfskin. The beam, from which the beamhouse derived its name, is a convex wooden slab sloping upward from the floor, at an angle of about 30°, to a point about three feet above the floor, which gives it a length of about six feet. The skin is thrown over the beam, grain side up.



Courtesy B. D. Eisendrath Tanning Co.

Fig. 130. Scudding Calfskins by Machine (foreground) and by Hand (background).

Leaning over the beam, the beamster pushes a specially designed, two-handled knife over the skin downward and to left and right, forcing the remnants of the epithelial tissues, glands, lime soaps, dirt and any remaining hairs out of the hair follicles and pores. Fig. 129 shows the typical beam knife. For ordinary work, he uses the concave edge of the knife, but when he desires to clear out some small area more difficult to scud or containing hair, he uses the convex edge. Beamsters must continually examine their knives and guard them against nicks that might scratch the skin.

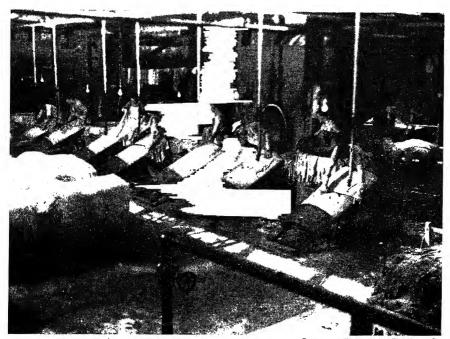
Scudding can usually be done better by hand than by machine because the hair follicles slope in many different directions. If the knife stroke is made in the direction of the hair, from root to tip, the dirt in the follicles is easily squeezed out,



Fig. 131. Section of Calf Beamhouse with Paddle, Liming Vats in Background and Scudding Machines in Left Foreground.

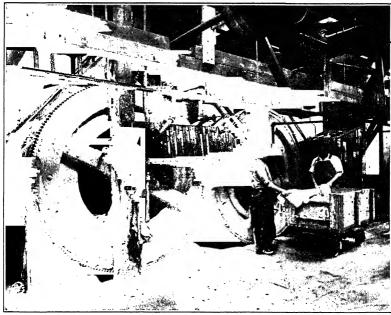
whereas there is a tendency for it to be trapped by a stroke in the opposite direction. There is a sufficient degree of transparency to a limed skin to enable the beamster to see the dirt and pigment in the follicles, and he directs his knife first one way and then another until the skin appears uniformly clean. He is also on the lookout for fine hairs not removed by the machine. The bulb of a new hair is as deeply seated as that of an old one, but there may not be enough of the new hair protruding above the surface of the skin to be gripped by the knives of the unhairing machine.

Hand-scudding, however, is an extremely laborious and disagreeable task and requires highly skilled labor. When tanneries are rushed, there is usually a shortage of skilled beamsters, and machine-scudding is far better than that of unskilled beamsters. It has become the practice in many tanneries to scud all the skins on a machine and then to inspect them individually, setting aside all the skins that do not pass inspection for the attention of highly skilled beamsters.



Courtesy The Ohio Leather Co.

Fig. 132. Beamhouse Showing Beamsters Scudding Calfskins by Hand.



Courtesy A. F. Gallun & Sons Corp.

Fig. 130 shows a scudding machine in operation on calfskins. It consists of a large, revolving drum with blades attached to its periphery. The operator places a skin grain-side up on a bolster which forces the skin against the moving blades. In the background can be seen the skilled beamsters who work over the skins that do not pass inspection.

Fig. 131 shows a section of the beamhouse of a calf tannery with the paddle vats used for liming in the background. The unhairing machines are shown in Fig. 103, Chapter 7, located behind the soaking vats. At the left, in Fig. 131 can be seen two scudding machines in operation. Skins can be unhaired and scudded better when they are warm, and it is customary to have tanks or barrels of water at 80° to 90° F. handy in which each skin can be dipped before scudding. Fig. 132 shows a battery of beamsters at work.

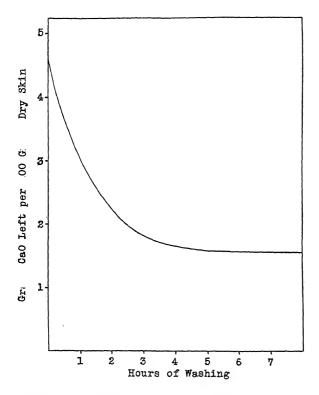


Fig. 134.

Rate of Removal of Lime from a Pack of Calfskins during Washing in Open-face Drum with Good Flow of Water.

Washing and Cheeking

After the skins have been scudded, they still contain much lime and soluble protein decomposition products, which it is desirable to remove at this stage. The scudded skins are made up into lots of about 1000 lbs. each and each lot is thrown into an open-face drum like those shown in Fig. 133. The drum revolves slowly while a heavy flow of water at 60° to 70° F. passes through and around the tumbling stock for 40 minutes, the overflow of water passing out through the open faces of the drums. The stock is then sent to be cheeked, or head-split.

The washing time of 40 minutes is not enough to remove all the lime that

can be removed by washing. The rate of lime removal with time can be seen in Fig 134, which was obtained by washing a pack of calfskin as described above, but increasing the washing time to 8 hours and taking out samples of skin for analysis at short intervals. The term CaO simply means lime expressed as calcium oxide, or unslaked lime.

The 40-minute washing is desirable because it removes some lime and also some protein decomposition products. Extending the time of washing is not desirable because it tends to make the stock loose.

At this stage, the stock usually has cheeks, heads and necks much thicker than the rest of the skins, and it is desirable to reduce their thicknesses more nearly to conform to that of the skins as a whole. This is done on a cheeking machine like that shown in Fig. 135.

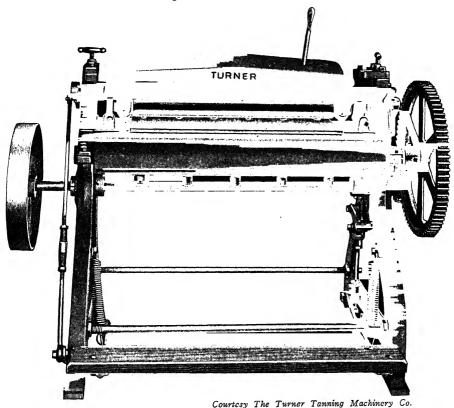


Fig. 135. Cheeking Machine for Leveling Cheeks, Heads and Necks of Raw Stock before Tanning.

The head end of each skin is put into this machine and, upon stepping on the treadle, the portion of the skin in the machine is drawn between a knife and gauge roll by a cast-iron grip roll having large finger slots along its entire length. The thickness of these heavier portions of the skin can thus be reduced to any desired thickness. The split obtained is usually thrown into glue stock. After cheeking, the raw stock is ready for deliming and bating, as described in Chapter 9.

Other Sharpening Agents in Liming

Sodium sulfide and hydrosulfide are not the only materials used to *sharpen* the limes, which means to increase the unhairing action without harm to the true skin. In actual use, sodium sulfide may be looked upon simply as a mixture of sodium hydrosulfide and caustic soda.

Arsenic

One of the first sharpening agents ever used in liming was arsenic disulfide. It was mixed with the lime before slaking in the proportion of about one part of the sulfide to 25 parts of the lime. Upon slaking with water, the resulting products were calcium hydroxide, calcium hydrosulfide and calcium sulfarsenite. Lime liquors sharpened with this mixture do not cause the skins to swell so much, and smoother leather is obtained than when using ordinary sodium sulfide. The reason for the lesser swelling with the arsenic mixture is that no caustic soda is formed and the solubility of the lime is decreased by the presence of the calcium hydrosulfide and the calcium sulfarsenite. The real unhairing agent in the mixture is apparently the calcium hydrosulfide.

Years ago many calfskin tanners replaced arsenic disulfide by sodium sulfide because the latter was speedier in its action, and with it skins could be unhaired after only one day in the lime liquor as against from 3 to 5 days with arsenic. They minimized the effect of the caustic soda present by using less sodium sulfide and raising the temperature of the lime liquors. Raising the temperature of the limes not only greatly increases the unhairing action, but it also decreases the solubility of the lime and, therefore, the pH value of the liquors. A calfskin suffers less damage when limed for 1 day at 82° F. than it does in 3 days at 70° F., although the amount of damage done in a fixed length of time increases with the temperature.

Calfskins, being from baby animals, are much more susceptible to damage in liming than goatskins, which are from mature animals. Since the longer time of liming required with the use of arsenic produced but little damage, many goatskin tanners have continued to use arsenic because of the smoother leather obtained than when using ordinary sodium sulfide. Now that hydrosulfides less caustic than sulfides have become available, even goatskin tanners are using them because they have all the advantages and none of the disadvantages of arsenic, are speedier in their action and much cheaper.

Dimethylamine

It has long been known that the unhairing action of lime liquors is increased by the use of old liquors that have previously been used for unhairing skins. Working under the auspices of the Tanners' Council of America, McLaughlin and his co-workers studied old lime liquors and the action of amines. They found that certain purified amines exert powerful unhairing actions when added to fresh lime liquors. In 1927, McLaughlin, Rockwell, O'Flaherty and Highberger applied for a patent on the use of amines for unhairing. U. S. patent No. 1,785,092 was granted them in December, 1930 and assigned to the Tanners' Council.

In the course of further investigation of the action of the various amines, it was found that monomethylamine, while a good material, was approximately only half as effective as dimethylamine, while trimethylamine was almost entirely without effect. This showed that the successful commercial application of methylamine in unhairing depended, in large measure, upon the economical production of a pure dimethylamine. The purity of the dimethylamine was important also for the reason that impure products have a pronounced disagreeable odor. Today, dimethylamine

is available in the form of a solution of dimethylamine sulfate containing less than a percent of other amines.

The commercial use of dimethylamine in unhairing has established the fact that it offers a means of unhairing in a short time with a minimum of plumping and destructive action on collagen.

Although sodium hydrosulfide contains no caustic soda, some caustic soda is formed whenever any sodium salt is added to a lime liquor. The amount formed with sodium sulfhydrate is very much less than is obtained with sodium sulfide, but dimethylamine cannot form any caustic soda when added to a lime liquor. Because of the absence of caustic soda in lime liquors sharpened with dimethylamine, the grain is kept very smooth, the flanks hold up better and the leather has better cutting value.

The dimethylamine sulfate of commerce contains 36 to 37 percent by weight of dimethylamine. It is used in the same manner as the liquid sodium hydrosulfide, but in amounts varying from $1\frac{1}{4}$ to $2\frac{1}{2}$ percent of the weight of the stock.

Sodium Cyanide

When sodium cyanide is added to lime liquors, it exerts a marked unhairing action on skins. The writer has been informed that several tanneries use sodium cynanide as the sharpening agent in liming as part of their regular procedure. Although sodium cyanide is very poisonous, precautions can be taken against its doing any harm in practice. Tanners using it are apparently unwilling to divulge the details of their procedures. Since the writer has had no experience with it, he can only refer the reader to the papers by Theis and Goeller included among the references listed at the end of this chapter.

Liming Goatskins

Goatskins are of such variety, and differ so greatly in their sensitivity to the unhairing action of lime liquors, that no single procedure can be laid down that will satisfactorily include all types. One generally satisfactory method is as follows: A pack of 1600 lbs, dry weight is soaked for 3 days according to the procedure given in Chapter 7. A 2500-gal, paddle vat is filled with water and then 400 lbs. of hydrated lime and 25 lbs. of liquid sodium hydrosulfide are added and well mixed. The pack is dumped into this liquor and the paddle is run while heating the liquor to 82° F. Every 6 hours, the paddle is run while the liquor is being reheated to 82° F. The paddle is run only while heating and the stock is left in the liquor only long enough to bring it to the state where it can be unhaired easily, which is usually from 2 to 3 days. The stock is then hauled out, unhaired on the machine and then fleshed. Batteries of paddle vats used for both soaking and liming goatskins are shown in Fig. 112 of Chapter 7. Fig. 136 shows both the unhairing and fleshing operations. In the background to the left an operator can be seen working on the unhairing machine. In the middle foreground, an operator is fleshing unhaired stock.

Some goatskin tanners scud the stock immediately after the fleshing operation, but others scud only after bating. Calfskins are always scudded before bating because fine hairs that can easily be scudded out before bating resist removal tenaciously after bating. Moreover, calfskins are very susceptible to damage in the bated condition, while goatskins, being of a harder nature, are much more resistant. After fleshing or scudding, the goatskins are washed in running water in a drum for 40 minutes and then sent to be delimed and bated.

Some goatskin tanners prefer to do most of their soaking in the lime liquors

They fear the danger of bacterial damage in long soaking and do not use caustic soda in soaking or liming for fear that an excessive amount might overswell the stock and cause rough grain. They also avoid using ordinary sodium sulfide in the lime liquors because of the caustic soda that it produces.

One method employed by such tanners is to soak the dry stock in a still-vat of water at 75° F. for 24 hours. The stock is then washed in a revolving drum with running water at 75° F. for one hour. The drumming causes a flexing of the stock which greatly assists the absorption of water by the stock. The stock is then put through a fleshing machine of the type shown in Fig. 104, Chapter 7. This removes very little flesh, but serves to *break* or soften the stock, making it more receptive to the absorption of water.

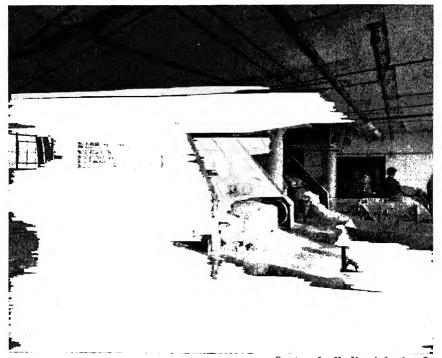


Fig. 136. Unhairing and Fleshing in Goatskin Tannery.

The stock is then limed for 14 days as follows: Two still-vats are used. One is made up fresh with water at 75° F., a great excess of hydrated lime and just enough arsenic disulfide to bring about easy unhairing in 14 days. The other liquor is exactly the same, but has been used for liming a previous pack for 7 days. More hydrated lime, but no more arsenic, is added to the used liquor. After mixing well, the stock is put into it and allowed to remain for 7 days. The stock is then pulled out, the liquor being run to the sewer, and put into a fresh liquor and left for 7 days. The stock is then unhaired, fleshed, washed and sent to be bated. The liquor used once is then used to receive another pack for the first 7 days.

Another method in use is to put the soaked skins into a paddle vat containing per 100 lbs. dry weight of goatskins to be limed 20 lbs. of hydrated lime and 1½ lbs. of dimethylamine in 800 lbs. of water (96 gals.) at 80° F. The pack is left in the liquor until ready for unhairing (about 6 days) and the paddle is run for only 10 minutes each morning and evening. Some tanners shorten the time of liming by adding soda ash to the liquor. When soda ash is added to a lime liquor, it causes a precipitation of calcium carbonate with the formation of caustic soda, which swells the stock and increases the unhairing action. By adding 1½ lbs. of soda ash per 100 lbs. dry weight of stock on the first day and 1½ lbs. more on the second day, each time while the paddle is running, the time required for unhairing is reduced to from 3 to 4 days.

The 3-day liming procedure, using sodium hydrosulfide, can also be applied to kangaroo skins and to dry calfskins.

Liming Heavy Hides

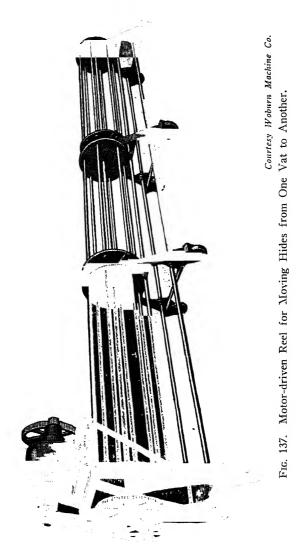
Heavy, green, salted hides can be limed and unhaired exactly like green, salted calfskins except for the quantities of materials used and the time of liming. Heavier hides contain more protein and less water per unit total weight; they should therefore be given more water and other materials per unit total weight and the time of liming may have to be extended to as much as 3 days or longer. In any case, the stock should always be taken from the lime liquor just as soon as it can be unhaired easily. It should be remembered that the raw stock continuously loses valuable hide substance all the time it is in the lime liquors at all practical temperatures. With increase of temperature easy unhairing is brought about in a shorter time, but the rate at which hide substance is lost also increases. Calfskins can be unhaired in 1 day by raising the temperature to 82° F. Although the rate of loss in hide substance is thereby increased, the total loss in 1 day at 82° F. is less than the loss in 3 days at 70° F. By using larger amounts of sodium hydrosulfide, the time of liming can be shortened. If the stock is hauled out just as soon as it can be unhaired easily, there will be less loss of hide substance than when less sodium hydrosulfide and a longer time of liming are used. If a great excess of hydrosulfide is used, the hair will be destroyed, but the stock itself will not be damaged. Since tanners find a ready market for hair, it is desirable not to damage it; consequently, the best amount of sodium hydrosulfide to use is the largest amount that causes no damage to the hair. The most important point to remember is that the stock should be taken from the lime liquor just as soon as it can be unhaired easily.

Liming Hides for Sole Leather

Manufacturers of sole leather are desirous of producing leather that is tight and solid in structure, having a fine, smooth grain surface and that can be rolled out flat without any distortions. When heavy steer hides are plumped by lime, any violent mechanical action on them may produce permanent distortions and looseness of the stock that would lower the value of the finished leather. Excessive swelling, as with caustic soda, is also avoided because it produces a grainy condition that mars the appearance of the finished leather. Many tanners of sole leather treat their heavy steer hides more delicately than do tanners of fine calfskins. Where ordinary sodium sulfide is used, the amount is less than that used for calfskins because of the damaging effect of the caustic soda. With sodium hydrosulfide, the amount can be increased to any extent desired to get easy unhairing in the time allowed.

A typical liming system contains as many rows of vats as there are backs of

hides to be limed each working day. Each row contains 10 vats, only 5 of which are used for liming. Each vat is 8 ft. long by 7 ft. wide by 8 ft. deep. Each pack weighs 5000 lbs. (about 83 hides weighing 60 lbs. each). After the hides have been soaked one day and fleshed, as described in Chapter 7, they are tied together



in a long chain, the two hind shanks of one hide being tied to the two fore shanks of the next. In this way, the long chain of hides is reeled from one vat to another. A typical lime reel is shown in Fig. 137. This reel is made to set over 3 rows of vats at one time, but can be obtained to set over only one or two rows.

The first hide in a chain is lifted onto the reel, the motor is turned on and

the reel starts rotating, pulling the entire chain of hides from one vat to the next one in the series.

The first 4 vats in the system contain only fresh water at 52° F. After one pack has been in one of these vats one day, it is reeled over into the next vat, the used water is run to the sewer and replaced by fresh water at 52° F. Each pack is reeled from one vat to the next each working day. The 5th, 6th, 7th, 8th and 9th vats contain hydrated lime and sodium hydrosulfide. In making up a new series, fill each of the 5 lime vats with 1900 gals. of water at 70° F. and add 100 lbs. of hydrated lime and 5 lbs. of liquid sodium hydrosulfide. Then each time a pack is reeled out of a vat, add to that vat 80 lbs. of hydrated lime and 4 lbs. of



Fig. 138. Mixing Hydrosulfide, Lime and Water for Use in Liming.

liquid sodium hydrosulfide. When 15 packs have been through any one vat, run the liquor to the sewer, clean the vat thoroughly and make up a fresh lime liquor by adding 200 lbs. of hydrated lime and 10 lbs. of liquid sodium hydrosulfide in 1900 gals. of water at 70° F. After starting a new system, the first vat to be cleaned will be No. 5, which is the first lime vat in the row. After the 15th pack is reeled out of it, the liquor should be run to the sewer, the vat cleaned and fresh liquor made up. For a new system, vat No. 6 should not be cleaned until the 18th pack has been reeled out of it, vat No. 7 when the 21st pack has been reeled out of it, vat No. 8 when the 24th pack has been reeled out of it and vat No. 9 when the 27th pack has been reeled out of it. Thereafter each vat should be emptied, cleaned and made fresh each time 15 packs have passed through it since the last cleaning.

In this way, the stock passing through receives an average of 10 lbs. of hydrated lime and $\frac{1}{2}$ lb. of liquid sodium hydrosulfide per 100 lbs.

It is customary to mix the hydrated lime and liquid sodium hydrosulfide with enough water so that it will flow easily, and then to dump it into the vat after the lot to be moved forward has been reeled out and before the next lot has been reeled in, mixing thoroughly before the new lot is reeled in. Fig. 138 shows one method of mixing the lime, hydrosulfide and water before adding to the vat. The mixing is done in the portable tank equipped with a high-speed electric mixer. The tank is equipped with an outlet valve for emptying into the vat.

A temperature of 70° F. is used because the period of liming is 5 days. By raising the temperature to 82° F., the time of liming can usually be cut to 3 days, but this should not be done unless the stock is actually taken out and unhaired in 3 days. It should be accepted as a fundamental rule always to remove stock from the limes just as soon as it can be unhaired easily. If the stock is limed for 5 days at 82° F., it will become loose in structure.

Warm-water Pool

Vat No. 10 in the system contains only fresh water at 90° F. made up fresh for each pack. After each pack is reeled from vat No. 9 into vat No. 10, it is left there for only 2 to 3 hours. As each hide is removed from vat No. 10, it is detached from the chain and moved directly to the unhairing machine, where it is unhaired.

The chief object of the warm-water pool is to warm the stock to a temperature between 80° and 90° F., although it does conveniently remove some of the excess lime. When hides are ready for unhairing, it has been found that the hair can be removed more easily and cleanly when their temperature is raised above 80° F. Even for light skins, it is customary for the beamster to dip each skin into warm water before scudding it. Great care should be exercised in seeing to it that stock is not left in the warm-water pools longer than is necessary to warm it completely through. If the stock is left in the warm water over night, valuable hide substance is lost and the stock becomes loose.

After the stock has been unhaired, it is washed in running water at 70° F. in an open-face drum for 10 minutes; excessive drumming must be avoided. Next it is fleshed on a machine and then hand-fleshed, trimmed and scudded on the beam. After this, it is sent to be bated.

It will be noted that each pack of hides passes successively through all 10 vats of the system, moving from one vat to the next each working day. The first 4 vats contain only fresh, cold water, the next 5 contain lime and the 10th vat only fresh, warm water.

Enzyme Unhairing

Following his development of the enzyme bate, Röhm discovered that an unhairing action on hides and skins can be effected by the use of pancreatic enzymes, provided the epidermis is first swollen by the application of solutions of caustic soda. Subsequently, the Röhm & Haas Company developed a commercial enzyme-unhairing agent under the name of "Arazym," which has found favor with some goatskin tanners. The writer has studied the action of pancreatic enzymes on soaked calfskins and obtained satisfactory unhairing when the epidermis was previously swollen with acid or alkali and rendered permeable to the enzyme. The method requires careful control for good results, but it is being used with some success in the unhairing of goatskins.

The following procedure is typical for goatskins, but variations must be made for different types of goatskins if the best results are to be obtained. Put a pack of 1600 lbs. of dry goatskins into water at 70° F. and let stand over night. Then run the paddle and wash in a good flow of running water for 20 minutes. Then add 32 lbs. of caustic soda and 80 lbs. of anhydrous Glauber's salt (sodium sulfate) previously dissolved in water and run the paddle for 10 minutes, keeping the temperature of the liquor close to 70° F., and let stand over night. Next morning run the paddle for 30 minutes while adding slowly 48 lbs. of caustic soda previously dissolved in water. Run the paddle for 30 minutes after the last addition and let stand for 3 hours. Then with the paddle running, add 48 lbs. more of caustic soda, previously dissolved in water, over a period of 30 minutes, run the paddle 30 minutes longer, and let stand until evening. Then run the paddle for 2 minutes and let stand over night.

Next morning run the paddle and wash the stock in running water at 75° F. for 1 hour. Leave the paddle vat filled with water at 75° F. and add slowly, with paddle running, 160 lbs. of sodium bicarbonate dissolved in 200 gals. of water at 75° F. Run the paddle for 10 minutes longer, add 32 lbs. of Arazym-CN, run the paddle 10 minutes longer and let stand until evening. Then run the paddle for 2 minutes and let stand over night. Next morning haul out the stock, unhair and flesh, wash in running water for 40 minutes and send to be bated.

The amounts of materials used must be varied according to the nature of the stock, using more for those of a hard nature and less for those of a soft nature. In the foregoing procedure, instead of adding 160 lbs. of sodium bicarbonate (10 percent of the dry weight of stock), it has been found preferable in some cases merely to lower the pH value of the liquor to 9.0 (as determined by Thymol Blue indicator) by adding about 3 percent of bicarbonate and running the paddle for 10 minutes. The pH value is then raised to 10.0 (as determined by Oleo Red indicator) by adding from $1\frac{1}{2}$ to 2 percent of caustic soda. The paddle is then run for 10 minutes and from $1\frac{1}{2}$ to 3 percent of Arazym-CN added, according to the nature of the stock.

Unhairing by Dissolving the Hair

During the World War, when the demand for shoe-upper leather for army shoes was at its peak, the writer developed a method for speeding up production by dissolving the hair of cow hides in strong solutions of sodium sulfide. The method follows: For each pack per day, select two 2500-gal. paddle vats side by side. Fill the first one with 420 lbs. of 60 percent sodium sulfide contained in 1900 gals. of water at 70° F. Into this liquor, dump a pack of 5000 lbs. of soaked cow hides and run the paddle for 1 hour. Let stand, and run the paddle for 2 minutes out of each hour until the stock has been in the liquor for 6 hours. Fill the second paddle vat with 420 lbs. of calcium chloride in 1900 gals. of water at 70° F.

After 6 hours in the sulfide liquor, the hair has become pulped and largely dissolved. With long, metal tongs, drag each hide from the sulfide liquor into the calcium chloride liquor. After all the stock has been moved over into the calcium-chloride liquor, run the paddle for 1 hour and let stand over night. Next morning run the paddle for 1 hour, haul out the stock, scud it on the unhairing machine and then wash in running water in the open-face drum for 40 minutes. Then send to be delimed and bated.

The sulfide and calcium chloride liquors can each be used for 10 packs of hides. For the second pack in the sulfide liquor, add 140 lbs. of 60 percent sodium sulfide and run as for the first lot. For the second pack in the chloride liquor, add 140 lbs. of calcium chloride and run as for the first lot. Continue this until 10 packs have been through both liquors. Then run the liquors to the sewer and start over.

When it is urgent, production can be doubled by putting a pack into the sulfide liquor in the evening and transferring it to the chloride liquor early in the morning, after the previous pack has been hauled out. The new pack is then hauled out of the chloride liquor in the evening to make room for the next lot, which has been in the sulfide liquor during the day. Millions of hides have been unhaired in this way with perfectly satisfactory results. The chief objection to this procedure is the loss of the hair, which the tanner ordinarily sells as a by-product. The method is still widely used on pigskin strips and other stock having hair of little or no value, or when speeding up production more than compensates for the loss of the hair.

The method cannot safely be used for fine calfskins because of the action of the caustic soda formed from the hydrolysis of the sodium sulfide. However, a satisfactory method has been developed for calfskins, which is as follows: Into a 2500gal, paddle vat, run a liquor of 340 lbs, of 100 percent calcium hydrosulfide and 170 lbs. of hydrated lime in 1900 gals. of water at 70° F. Dump 5000 lbs. of soaked calfskins into this liquor and run the paddle for 30 minutes. Then run the paddle for 2 minutes each hour until the hair is sufficiently pulped to permit clean scudding on the unhairing machine. This may take several hours, but the stock should be pulled out as soon as ready. Scud on the unhairing machine, wash in the openface drum for 40 minutes with running water at 70° F., check and send to be delimed and bated. The writer has used this method on hundreds of thousands of calfskins with results fully as good; if not actually better than those obtained with small amounts of hydrosulfide, according to the procedure described above. The only disadvantages were the loss of the hair and the necessity for manufacturing the calcium hydrosulfide by passing hydrogen sulfide gas into suspensions of hydrated lime in water. In such liquors the stock does not become plumped, as in ordinary liming, but more fallen, as in bating. It is possible that this method may be revived by the commercial production of calcium hydrosulfide.

Dewooling Sheepskins

Sheepskin tanners usually purchase their raw stock already dewooled, bated and pickled, excepting when they are producing garment leathers with the wool left on. A good method for use in the packing house is as follows: As the skins are dropped from the killing floor, spread them out to cool and then make them up into packs of 5000 lbs. each. Put each pack into a 2500-gal. paddle vat filled with water at 52° F. After all the skins are in, run the paddle for 2 minutes and then let stand for 5 hours. Then wash in running water at 52° F. for 30 minutes and let stand over night in water at 52°F. Then haul out the stock and allow it to drain. Make up a sulfide paste as follows: Mix 100 lbs. of hydrated lime with 18 gals, of water and add 12½ lbs. of liquid sodium hydrosulfide and mix intimately. Then take the drained skins, one by one, and lay them out flat on a table, flesh side up. Coat the flesh side heavily with sulfide paste. Then fold the skin along the line of the backbone so that the flesh side of one side coincides with that of the other side, taking care not to get any sulfide paste on the wool. Then hang each skin from the tail, head down, in a room at about 80° F. and leave over night. During the night the hydrosulfide diffuses through the skin to the epidermis, where it dissolves the cells of the Malpighian layer and loosens the wool. Then throw each skin over a beam and work the wool off with a beam knife, scudding the skin at the same time.

After the whole pack has been dewooled, put it into a 2500-gal. paddle vat containing 150 lbs. of hydrated lime in 1900 gals. of water at 82° F. Run the paddle

for 30 minutes and let stand over night. Next day, scud the skins again over the beam and wash in running water in a paddle vat for 30 minutes. Then delime, bate and pickle according to the procedures given for calfskins in Chapter 9, except for the amount of acid used in pickling. In pickling sheepskins, it is customary to use enough sulfuric acid so that the used liquor after pickling will contain 1½ oz. of sulfuric acid per gal. of pickle liquor. After draining from the pickle, the skins are bundled for shipment to the tanneries.

It will be recalled from Chapter 1 that sheepskins have a very loose structure. They are readily damaged by violent mechanical agitation and so care should be taken to reduce mechanical agitation to a minimum in all operations.

If the animals are not slaughtered in the larger packing houses, the skins are usually cured with salt and sold to wool-pullers, who put them through operations similar in principle to those described above. Both packers and wool-pullers sell the wool in the wool markets and the pickled skins to the tanners. Occasionally tanners may find it to their advantage to do their own dewooling and will find the foregoing procedure quite satisfactory.

Sweating

The writer's justification for including the *sweating* method of unhairing skins in a book on modern practice is that it is probably the oldest method known for unhairing and apparently is still practiced in some countries, particularly for sheepskins. It received the name sweating from the nature of the process in its more highly developed state. It consists of little more than the putrefaction of the cells of the Malpighian layer. Since it is only necessary to allow a fresh skin to remain for a day or two in a warm, damp place to cause a loosening of the hair, the method was probably discovered very early in the history of the human race. It is not improbable that the accidental discovery of this action first revealed to the ancients the advantages of unhaired skins for certain purposes.

Because of the danger of serious damage to the skins in the sweat chambers, unless the process was very carefully watched and controlled, it ceased to be popular for the best grades of skins after safer methods of unhairing were devised. It is still in use in some tanneries for the lower grades of skins, such as the cheaper classes of dried hides and sheep skins where the wool is valued more highly than the skin.

The skins are generally hung from beams in a closed room in which the air is kept warm and humid. The temperature, humidity, and ventilation must be carefully controlled. During the process a considerable quantity of ammonia and amines are evolved and these assist in the unhairing action. Just as soon as the hair slips easily, the skins are removed from the sweat chamber and dumped into saturated lime water. The lime water serves to retard further bacterial action and to cause the skins to swell somewhat by absorption of water; the skins upon coming from the sweat chamber are in a very flaccid and slimy condition.

Wilson and Daub made a study of the sweating process under the microscope. Pieces of fresh sheep skin were kept in a closed receptacle having an atmosphere saturated with water vapor at about 100° F. At frequent intervals strips of skin were removed for sectioning and examining under the microscope. At the end of 42 hours, the wool could be rubbed off with ease and the skin had apparently suffered no damage. The odor of ammonia in the receptacle after the first day was very pronounced.

The first sign of action visible under the microscope was the separation of the cells of the Malpighian layer from one another and from the surface of the derma.

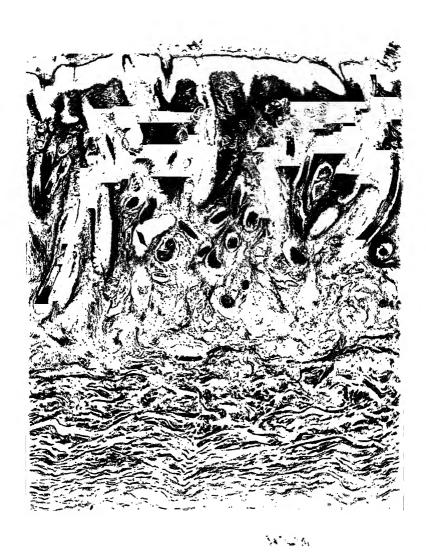


Fig. 139. Vertical Section of Sheep Skin after 42 Hours in Sweat Chamber.

Location: butt.

Thickness of section: 20 microns, or 0.00079 inch.

Magnification: 45 diameters.

This action gradually spread to the outermost layers of cells of the sebaceous and sudoriferous glands. On the second day the action had proceeded so far that the epidermis, glands and wool were completely separated from the derma and many



Fig. 140. Vertical Section of Thermostat Layer of Sheep Skin after 42 Hours in Sweat Chamber.

Location: butt.

Thickness of section: 20 microns, or 0.00079 inch. Magnification: 135 diameters.

of the epithelial cells had completely disintegrated. A section of the skin after being in the sweat chamber for 42 hours is shown in Fig. 139. The upper portion of the section is shown in Fig. 140 at a much higher magnification.

It will be noted that the corneous layer is still intact, but the Malpighian layer

has almost completely disintegrated, the linings of the hair follicles are broken up, and the glands have all been loosened and separated from the derma. Fig. 139 should be compared with Fig. 28 of Chapter 1, which represents a section from the same skin fixed in Erlicki's fluid within an hour after the death of the animal.

In practice, the systematic cleaning of the sweat chambers is necessary in order to prevent the increase of undesirable organisms that may be carried in from time to time. Hampshire investigated the cause of a pitting, or liquefaction in spots, of the grain and flesh surfaces of sheep skins, a damage known to the trade as run pelts. He found that the pittings was caused by several species of wormlike organisms belonging to the family Nemathelminthes and growing to a length of about one millimeter. Apparently they are killed by simple drying. They were found in great numbers in the sweat chambers, but not on skins which had not yet entered the chambers. In laboratory experiments, they produced a pitting of the skin in the presence of a small amount of ammonia, such as is always present in the sweat chambers. It was found that uniform slipping of the wool could be produced by incubating the skin in a clean vessel which excluded all organisms other than those present on the incoming skin, and skin treated in this way was free from pitting. It would seem that the danger of run pelts can be completely avoided by making certain of the cleanliness of the sweat chamber before the skins enter.

Upon coming from the sweat chamber, the skins are usually thrown into saturated limewater containing an excess of lime, which checks the bacterial action. They are left there over night and then taken out, unhaired, scudded, washed and sent on to be delimed and bated.

No attempt has been made to cover all possible procedures for unhairing or all known unhairing and sharpening agents. It is believed that the procedures outlined fully portray the principles of modern practice. The unhairing action of acids has been used in an experimental way and hydrochloric acid has been used in the removal of the shagreen, or epidermal layer, of shark skins. Skins can be unhaired after only 2-hours' contact with ammonia water at pH values between 11.7 and 12.0, but the method has not been considered practical.

All kinds of dry stock, having been soaked before liming, behave much like green, salted stock except for being more resistant to the action of the lime and the sharpening agents. For dry stock, the time of liming and amounts of sharpening agents are usually increased.

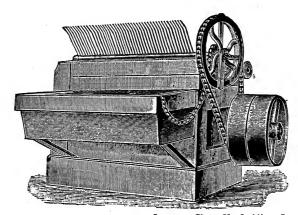
Lime obtained from different sources varies in composition according to the limestone from which it was produced. Many tanners claim that they get different results from lime obtained from different sources. The writer carried out a long series of tests on a large scale, comparing pure hydrated lime with Wisconsin dolomite lime, which contains about 38 percent of magnesium oxide. The results obtained over a period of years favored the pure hydrated lime, but the actual difference in practical result was so small that it was necessary to extend the comparative tests over a period of years to come to a definite conclusion. Impurities in any materials used in the tannery are undesirable and the writer has always advised tanners to buy the purest hydrated lime available to them.

For calfskins, where the volume of liquor is sufficient to allow free movement of the stock during paddling, the writer has found that 3 lbs. of hydrated lime per 100 lbs. soaked weight of stock gives the best results. If still vats are used or if the vats are crowded, more must be used. In sole-leather tanneries, where paddles are generally not used, it is customary to use about 10 lbs. of hydrated lime per 100 lbs. of soaked steer hides. It is desirable to avoid any

great excess because it is wasteful and makes the deliming operation more difficult.

By-products

The by-products from the beamhouse are hair, trimmings and fleshings, and grease. The trimmings and fleshings from calfskins are sold to manufacturers of gelatin. Those from heavy hides are sold to manufacturers of glue. Sheepskin tanners often recover and sell the grease obtained from the degreasing operations. Nearly all tanners find a ready market for the hair. It is now customary to wash and dry the hair before offering it for sale. Fig. 140 shows a typical hairwashing machine.



Courtesy Chas. H. Stehling Co. Fig. 141. Hair-washing Machine.

Some communities require the screening of beamhouse sewage before running to the sewers. The screenings and worthless fleshings are usually pressed, dried and burned. It seems likely that the day will come when all tanners will be required to treat their sewage before running it to the sewers.

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Chapter 9

Bating

Historical Development

Until after the beginning of the twentieth century, bating was the most curious of all the operations of the tannery. For centuries it had about it an atmosphere of mystery and a fetid aroma, but it was universally used. It was not only a disgusting operation, but it was so completely enshrouded in secrecy, and so jealously guarded, that it has not been possible to trace its origin. However, the process as handed down from generation to generation of tanners is still an unpleasant memory to many tanners living today. It consisted in digesting the limed and unhaired skins in a warm infusion of the dung of dogs or fowls until all plumpness had disappeared and the skins had become so soft as to retain the impression of thumb and finger when pinched and sufficiently porous to permit the passage of air under pressure. When hen or pigeon manure was used, the process was called bating, but when dog dung was used, it was called puering. The hen or pigeon manure was generally used for heavy hides because it penetrates more rapidly than dog dung because it contains urea and the other urinary products. Tanners of light leathers used dog dung because of its milder action, and for that reason many of the older tanners of light leathers still refer to the operation as puering, even though the discontinuance of the use of dungs made the operation the same in principle and in materials used for all kinds of leathers. Since the term bating is now practically universal for all processes of digestion of the raw stock after unhairing, we shall accept it as the correct name for the operation.

A common method for treating light skins was to put them into a paddle vat filled with water at about animal body heat. The dog dung was usually first worked up into a cream with the hands, using a small amount of warm water, and allowed to "ripen" for a few days. After the skins entered the water, the paddle was started running and the creamed dung was added in the proportion of about one pound per gallon. After the addition of the dung, the skins were watched very closely and were pulled out just as soon as the bate master, or puer master, pronounced them done. To leave them in the liquor longer would result in putrefaction and ruination of the stock. The bate master was a very important man and rose to his exalted position only after many years' apprenticeship under a master. Without his expert judgment on when stock was properly bated, the manufacture of leather became an extremely hazardous undertaking, and a tanner could not hope to compete in the leather markets without an expert bate master. Properly bated stock produced leather of fine, smooth grain surface; but unbated stock had an unsightly appearance and feel that precluded its use where appearance was of great importance.

Once a good bate liquor was made up, it was used for many successive packs of skins, being freshened for each pack with new dung. Some bate masters claimed that good results could never be obtained with a perfectly fresh bate. In making an old bate liquor ready for a new pack of skins, the bate master knew just how much of the old liquor to run to the sewer and just how much new material

to add. He took as much pride in his *ripe* old liquors as a sportsman did in a fine breed of racing horses that he had raised.

Not all bate masters were infallible, and spoilage of stock in bating was enormous. With the advent of science, it was inevitable that sooner or later an extremely important, but hazardous and disgusting operation would be displaced by a more scientific one. The first difficulty was to learn just what was the active principle in dung responsible for the fine, smooth grain in properly bated stock; the second was to learn the nature of the action of this principle on limed and unhaired hides and skins. The modern tanner owes his freedom from the old hazardous and filthy bating operation to the work of two great men, both of whom it was the writer's privilege to know during their lifetimes, Joseph Turney Wood, of Nottingham, England, and Otto Röhm, of Darmstadt, Germany.

Mr. Wood worked in the tannery of his uncle, Sir John Turney, and to him was entrusted the responsibilities of the *puer shop*. In his book, Wood says "When learning the trade as an apprentice, every fault in the leather was attibuted to this part of the work and the troubles and miseries of the *puer shop* first caused me to take up the study of *puering*. I was determined to know the causes underlying the process. Puering is not only a filthy and disgusting operation, but is prejudicial to health, and in the nature of it is attended by more worry and trouble than all the rest of the processes in leather making put together."

The writer spent some time in Nottingham with Mr. Wood, having him recall his long and tedious labors in trying to discover the active principle in dog dung. In his extensive researches, he used three workshops: (1) a system of dog kennels, (2) his own puer shop at the tannery and (3) the chemical laboratories at the University of Nottingham. His painstaking analyses of dog dungs are now a classic.

After determining the presence of each constituent of dung, he studied its effect upon skins in the puer shop. All the simpler constituents gave only negative results when applied to skins. Positive and valuable results began to come only after he started to work on the bacterial and enzyme activities of the dung. His work indicated that the dung bates owed their activity to either pancreatic enzymes or to the enzymes secreted by bacteria.

In the hope of developing a commercial bate free from the filth of the dungs, he turned his attention to the development of bacterial cultures, many of which seemed very promising.

He recognized the importance of pH value in bating and was one of the first men ever to control pH value in an industrial operation. He was controlling it in the puer shop long before the measurement of pH value was being taught at many of the larger universities of the world.

About 1903 in Germany, another young chemist, Dr. Otto Röhm, had taken an active interest in the problem of bating hides and skins. As was natural from the knowledge available at the time, he tried to solve the problem by developing practical methods of deliming the stock. Complete deliming and neutralization of the stock produces the condition and feel used by the expert bate master to determine the completeness of bating. After years of long and disappointing experiments, he came to the conclusion that true bating required the action of enzymes along with the deliming.

It was very fortunate that in his younger days he had been employed by a pharmaceutical house and had become thoroughly familiar with the preparation of the unorganized ferments and with the conditions required for their optimum efficiency. Once he had determined that enzymes were necessary for the true bating action, his systematic researches led him quickly to the selection of the pancreatic enzymes.

On June 7, 1907, he applied for a patent covering the process of bating hides and skins by the use of an aqueous extract of the pancreatic gland plus a lime-dissolving salt, and German Patent No. 200,519 was granted to him on July 21, 1908. The product covered by this patent was trade-named "Oropon," and it was the first bating material that was ever really successful on a large, commercial scale as an improvement over the dung bates.

In his book, Mr. Wood commented on Dr. Röhm's achievement as follows: "An interesting application of the theory of the bating process which was put forward by me (J. S. C. I., 1898, p. 1013) is that of Dr. Otto Röhm in 1908, in which, instead of a bacterial culture, he employs an infusion of pancreas in conjunction with ammonium salts. This bate has been put on the market in the form of a powder under the name of Oropon."

After a great discovery has been made and put to universal use for the general good, historians become interested in determining to whom credit for the discovery is due; but great discoveries can rarely be attributed to the work of a single mind. It is to Mr. Wood's credit that he was the first to undertake a thorough and scientific study of the bating problem and it is to Dr. Röhm's credit that he was the first to develop a really successful commercial bate that replaced the filthy dungs by a clean product that was superior in its action and made possible the scientific control of the bating operation.

In the ordinary drying of the pancreatic glands, there is a great danger of decomposition, but they can be ground to liquid consistency and mixed with dry wood meal. If the proportion of wood meal to glands is sufficiently great, the result is a mixture of low moisture content which is essentially air-dry immediately after mixing and is not subject to decomposition. By mixing this with dry ammonioum salts, or other deliming agents, an air-dry powder is obtained that is easily handled and can be stored indefinitely.

Enzymes, not being single, pure chemical substances, are not measured by weight, but by their activities on some definite material. Since different enzyme activities were found desirable in bating different kinds of stock, it became customary to produce a series of Oropon products of predetermined enzyme activities, and each grade of Oropon was designated by a letter indicating its activity. As it was also found desirable to use different deliming agents for different types of stock, a letter was added to the name to indicate the deliming agent. Thus Oropon CS indicates that the enzyme activity corresponds to the standard designated as C and that the deliming agent is ammonium sulfate, designated by the letter S.

The commercial development of the Oropon bate was heralded by the entire leather world as probably the greatest scientific development in its history. The speed with which its use was universally adopted by one of the most conservative industries in the world shows how urgently it was needed. However, the simplicity of operation and control of bating with artificial materials has so completely removed the fears and hazards of the dung bates of 40 years ago that the younger generation of tanners is tending to lose sight of the great importance of the bating operation. Long after Oropon was in general use, there were many theories as to the actual mechanism of the bating operation. It may simplify the discussion of these theories to present first the writer's present method of bating calfskins.

Deliming and Bating Calfskins

In the course of their progress through the modern tannery, we left our calfskins after they had been unhaired, scudded, washed and cheeked. Put the

5000-lb. pack of skins into a 2500-gal. paddle vat filled with 1900 gals. of fresh water at 80° F. The pack will cause the vat to be filled practically to the 2500gal. mark. Have on hand a solution containing about 1 lb. of sulfuric acid to each gallon of water. Always pour the acid into the water; never pour water onto strong sulfuric acid because heat is rapidly developed which may cause acid solution to be spurted in one's face. Also have ready a pH comparator with methyl red indicator, like that described in Chapter 7. Start the paddle running and for the first lot run this way, make measurements of the pH value of the liquor every 5 minutes. After each measurement, if the pH value is above 5.0, add enough of the dilute sulfuric acid to bring it down to 5.0. Be extremely careful never to allow the pH value to drop below 4.7. Continue this until two successive readings of 5.0, five minutes apart, are obtained. The amount of acid required to bring about this equilibrium at a pH value of 5.0 will differ widely in different tanneries because of the great differences in lime content of the stock. In any one tannery, after the tedium of running the first few packs to approximate equilibrium, the process becomes simplified and shortened by a knowledge of the average amount of sulfuric acid required. In different tanneries, the amount of acid required may vary from 10 lbs. to over 50 lbs., depending upon the amounts of lime carried over by the stock, and the time required to reach approximate equilibrium may vary from 30 to 90 minutes. The paddle is run continuously.

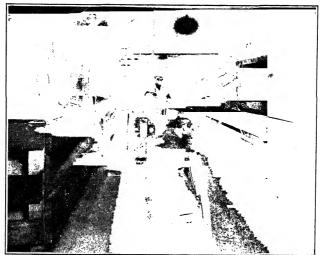
After this deliming operation, transfer the skins to a 2500-gal, paddle vat for bating. This is prepared for by leaving in the vat about 500 gals, of the liquor from the previous lot and adding 1400 gals, of fresh water and 40 lbs, of Oropon CS. The stock is thrown into this liquor and the temperature is raised, with the stock in, to 92° F. The paddle is run continuously for 90 minutes and the stock is hauled out. Although pH control of bating for stock already delimed is not absolutely essential, the writer has found a slight improvement in the stock by keeping the pH value of the liquor at 7.4 by adding occasional small amounts of sulfuric acid, using the pH comparator with the phenol-red indicator.

After the skins have been hauled from the bate liquor, they should be moved as quickly as possible to start the next operation, which is usually either pickling or tanning. They are washed for 2 minutes with running water in a drum before putting into tan or pickle liquor.

Actually the optimum time and temperature of bating and the optimum amount of Oropon to use vary with the nature of the stock. Winter skins and skins in poor condition are much more sensitive to these variables than good summer stock. The foregoing procedure was based on average results on millions of skins of all kinds, and has given almost universally good results in many different tanneries without adjustment. If a tanner is determined to make the finest calf leather possible with whatever stock he is using, he should make adjustments according to variations in the nature of the stock.

The writer has developed a satisfactory procedure for making these adjustments, although it is by nature time-consuming and somewhat laborious. The first adjustment to make is that of time of bating. After the stock has been in the bate liquor for 30 minutes, haul out one-fourth of the pack and take it to a place where each skin can be examined separately under a good light. It will be noted that some skins appear grainier than others. This grainy condition is observable as a delicate mosaic pattern of exceedingly minute depressions extending inward from the bellies. It is really the pattern of the blood-vessel system of the skin projected onto the grain surface. When this pattern is exaggerated, the skin is classified as grainy. After examing and grading all skins, the per-

centage of the total number of skins examined that are classified as grainy should be calculated. If the skins are to be pickled, it is better to make the examinations after pickling because the pattern is then more sharply defined.



Courtesy A. F. Gallun & Sons Corp.

Fig. 142. Bate Master Examing Calfskins During Bating.



Courtesy A. F. Gallun & Sons Corp. Fig. 143. Expert Workmen Classifying Calfskins after Bating.

At the end of 60 minutes of bating, the second one-fourth of the pack is hauled out and the percentage of grainy skins determined. The third one-fourth is hauled out after 90 minutes and the last one-fourth after 120 minutes. When the values for percentage of grainy skins become available, it will be found that

they follow a definite order. Usually the value for 30 minutes will be highest, that for 60 minutes lower and that for 90 minutes lowest and that for 120 minutes higher than for 90 minutes. However, for poor stock, it may be found that the value for 60 minutes is lowest; the tanner should then cut the bating time to 60 minutes, or else run another series using bating times of 50, 60, 70 and 80 minutes. By following this procedure intelligently, he can determine the optimum time for bating any particular class of stock. For some types of stock he may find the optimum at less than one hour and for others at more than two hours.

Having determined optimum time at 92° F., he may then determine optimum temperature and optimum percentage of Oropon, but he must be sure to vary only one factor at a time. He can also study the effect of varying pH value, but the writer has always found the optimum at about 7.4.

Fig. 142 shows a bate master examining calfskins during the bating operation and Fig. 143 examining and classifying skins after bating.

Mechanism of Bating

Artificial bates came into general use after it was shown that the active principal of the old dung bates consisted of *ensymes*. It was also recognized that the ammonium salts formed during bating played an important role. However, it was a long time after artificial bates were in common use that quantitative work was done to show just what the enzymes and ammonium salts did to unhaired hides and skins that caused the resulting leather to be so much finer and smoother than leather made without bating. A tanner may not be qualified to understand the chemistry of the many actions that occur during bating, but he can become familiar with what occurs without a knowledge of chemistry, and it is very important that he should do so.

The food eaten by many animals is digested in their small intestines by means of enzymes formed during the reproduction of the cells of the pancreas and emptied into the digestive tract. Similar enzymes are formed during the reproduction of bacteria and molds. Enzymes are complex chemical substances that act on many structural organic substances in the presence of water and at the right pH value, causing them to break down into simpler substances, which may be soluble in water. The pancreatic enzymes include amylases, which act on starchy bodies, proteases, which act on protein materials and lipases, which act on fatty materials. Wood found all three classes in dog dung. The most important protease for bating in the pancreas appears to be trypsin, an enzyme most active at a pH value of about 7.4. The writer has shown that the lipases of the pancreas are also important in bating and that they act vigorously at a pH value of 7.4. It is interesting to note that the normal pH value of the blood of healthy animals is about 7.4.

Of the things that happen during bating, there are at least 7 of sufficient importance to merit separate discussions; they are (1) removal of degradation products of the epidermal system, which include hair, epidermis, and glands; (2) hydrolysis of elastin fibers; (3) hydrolysis of collagen fibers; (4) falling; (5) regulation of pH value; (6) deliming and (7) bacterial action.

Removal of Degradation Products of Epidermal System

During the action of the lime liquors on the epithelial cells of the epidermis and on the sebaceous glands, degradation products are formed which remain in the hides and skins after unhairing, scudding and washing. They are present in the region just under the grain surface as viscous solutions or jellies adhering to the structures of the thermostat layer. They cannot readily be seen by examination

under a microscope, but they are precipitated as flocculent masses by contact with acid solutions. If a calfskin ready for bating is cut into sides along the line of the backbone, and one side is bated properly and the other put through a procedure that is identical except for the absence of the enzymes, they will appear much alike and have the same degree of flaccidity, but they will appear very different after pickling or tanning. The side not receiving any enzyme will have a very thick, spongy and irregular grain surface, suggesting the presence of keratose precipitated in the grain layer. As finished leather, it will have the unsightly appearance of unbated stock. By making careful comparative analyses of the two sides, the presence of much more nitrogenous matter can be proved in the side not receiving enzyme in bating. In titrating old lime liquors after filtering to determine their lime contents, the writer has often observed that a flocculent nitrogenous precipitate forms when enough acid has been added to make the liquor acid to methyl orange. It was shown that this precipitate comes from degradation products of epidermis and hair, known as keratose.

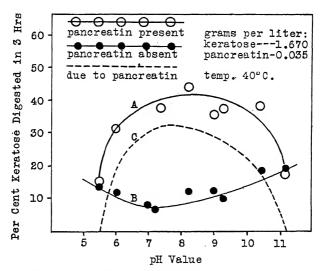


Fig. 144. Effect of pH Value on the Digestion of Keratose by Pancreatin.

Wilson and Merrill produced a purified keratose for study by first dissolving calf hair in strong caustic-soda solution, adding acid to bring the pH value down to 8.0, at which point the keratose is still soluble, filtering to get rid of the insoluble foreign matter, and then adding enough more acid to reduce the pH value to 4.1, at which point the keratose is precipitated quantitatively as a voluminous white mass. Over the pH range 5.5 to 11.2, they found that pancreatic enzymes rapidly break down keratose into water-soluble materials that do not precipitate upon acidifying the solution. It was shown quantitatively that the action of the enzymes on keratose was greatest over the pH range ordinarily used in bating. Without going into the details of their work, it will be sufficient to show some of the results. Fig. 144 shows the percentage of the keratose used in a series that was digested, or dissolved, in a period of 3 hours by the pancreatin at different pH values. Curve A shows the percentage digested in the presence of the enzyme, and Curve B the percentage digested in the absence of enzyme due to the treatment. Curve C shows

the percentage of keratose digested by the enzyme, obtained by subtracting values of Curve B from those of Curve A. The greatest action by the enzyme occurs between the pH values 7.2 and 8.0.

Fig. 145 shows the effect of time on this digestion. A commercial bate was used for comparison along with the pancreatin; the difference in the two curves merely represents the difference in enzyme activity between the pure enzyme and the commercial bate. The pure enzyme was a very expensive U. S. P. product. With no enzyme present, the digestion is very small. In the practical bating of

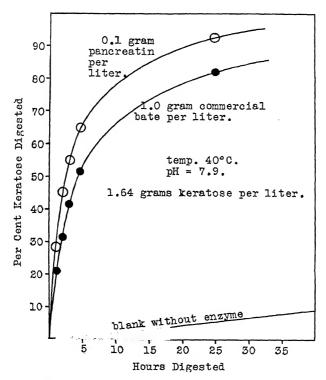


Fig. 145. Effect of Time on the Digestion of Keratose by Pancreatin and by a Commercial Bate.

hides and skins, it is probable that not all the keratose is removed; but it is likely that the bulk of the material that would form unsightly precipitates in the grain layer upon acidifying after the stock is removed.

This work did not deal with the degradation products of the sebaceous glands, but the writer has found it very desirable to have lipases present in the bate in order to get the finest leather. He has compared bates with small and with large proportions of lipases present and has obtained finer leather with the larger proportions. The writer now believes that the most important single function of bating is the removal of the degradation products of the epidermal system, particularly the keratoses and remnants of the sebaceous glands. And yet, the other functions are probably of measurable importance.

Hydrolysis of Elastin Fibers

It will be recalled from Chapter 1 that the elastin fibers in the skin perform a service in the grain layer of the skin like that of structural steel-work in a building. They follow a pattern in the grain layer which is essentially the same as that of the blood-vessel system. When a strip of gelatin is swollen by immersion in dilute solutions of acid or alkali, it swells by absorbing water, and the increase

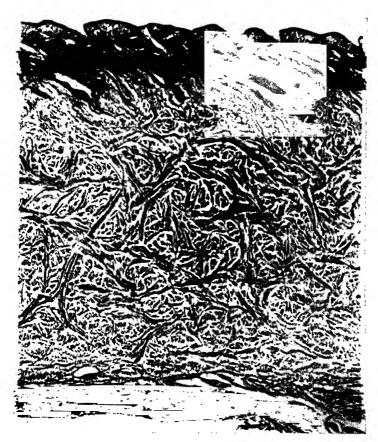


Fig. 146. Vertical Section of Calf Skin before Bating.

Location: butt.

Thickness of section: 40 microns, or 0.00158 inch.

Magnification: 35 diameters.

in size is proportional in all three dimensions. There is no reason to believe that the protein collagen behaves differently from gelatin in this respect. But when a hide or skin is swollen, there is little or no increase in area, but a great increase in thickness, accompanied by a distortion and the appearance of the pattern of the blood-vessel system on the grain surface in the form of depressions. Apparently the system of elastin fibers resists swelling and great tension is set up in the skin, causing the feeling of plumpness and the appearance of graininess.

One of the first fundamental actions attributed to bating was the removal of the elastin fibers, taking away the structural support in the grain layer responsible for the grainy condition accompanying any marked swelling of the skin. By the use of a microscope, Krall proved that the elastin fibers can be removed from skin by digestion in an infusion of dog dung at 40° C. (104° F.).

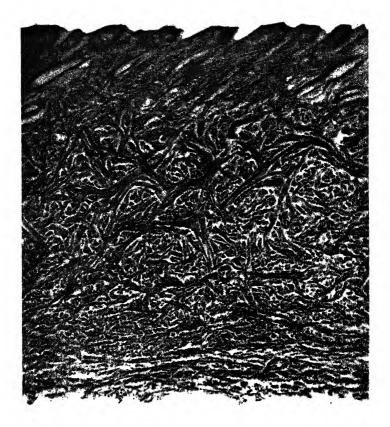


Fig. 147. Vertical Section of Calf Skin after Bating 24 Hours with Pancreatin.

Location: butt.

Thickness of section: 40 microns, or 0.00158 inch.

Magnification: 35 diameters.

In collaboration with J. T. Wood, Seymour-Jones carried out an interesting experiment on the bating of sheep skin. The "flywing" grain of a sheep skin was split from the main body of the skin, called simply flesh for convenience, and both grain and flesh were cut into halves along the backbone. One grain and one flesh were bated with pancreol, a pancreatin preparation similar to Oropon, while the other halves were delimed with acetic acid, but not bated. All four pieces were then tanned with sumac. There was comparatively little difference between the bated and unbated flesh halves, but the grain samples were very different from each other. The bated grain was soft and even, with the hair-holes clean and

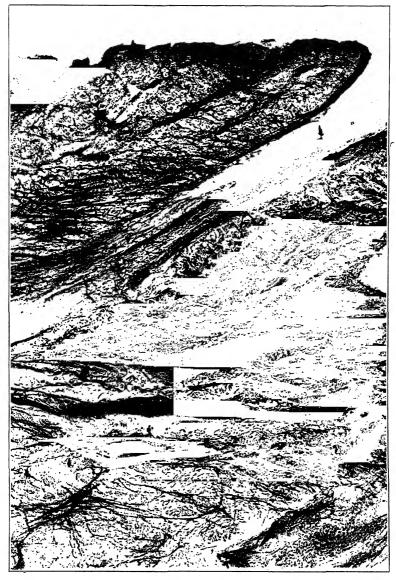


Fig. 148. Vertical Section of Grain Layer of Cow Hide before Bating.

Location: butt.

Thickness of section: 20 microns, or 0.00079 inch.

Magnification: 140 diameters.

clear, but in the unbated grain the hair-holes appeared to be glued up and the surface had a rough, contracted appearance. He concluded that elastin present in the region of the grain membrane must be digested before tanning in order to



Fig. 149. Vertical Section of Grain Layer of Calf Skin before Bating. Location: butt.

Thickness of section: 20 microns, or 0.00079 inch. Magnification: 140 diameters.

produce a satisfactory grain surface, but that the bating of the skin under the grain is not only unnecessary, but often undesirable.

Wilson and Daub made very extensive studies of the action of pancreatin upon the elastin fibers of calfskins. They made photomicrographs by a special technic to



Fig. 150. Vertical Section of Grain Layer of Sheep Skin before Bating.

Location: butt.

Thickness of section: 20 microns, or 0.00079 inch. Magnification: 140 diameters.

show the elastin fibers of the skin very clearly and then followed the fate of the elastin fibers by direct observation. Fig. 146 shows a vertical section of calfskin after liming, unhairing, scudding and washing. The elastin fibers can be seen in the grain and flesh layers stained a very dark color by means of Weigert's



Fig. 151. Vertical Section of Grain Layer of Hog Skin before Bating.
 Location: butt.
 Thickness of section: 20 microns, or 0.00079 inch.
 Magnification: 140 diameters.

resorcin-fuchsin dye and picro-red. Fig. 147 shows a similar section from the same skin taken after digesting for 24 hours at 40° C. with a solution of 0.1 gram of pancreatin per liter at a pH value maintained at 7.5 All the elastin fibers have been removed by the enzymes.

At higher magnifications, Fig. 148 shows the elastin fibers in the grain layer of a cow hide, Fig. 149 in the grain layer of a calfskin, Fig. 150 in the grain layer of a sheep skin and Fig. 151 in the grain layer of a hog skin.

Wilson and Daub studied the effect of pH value on the removal of elastin from calf skins by estimating with the eye the removal as seen under a microscope. The results are shown in Fig. 152.

For the smaller amount of enzyme, complete removal of elastin occurred only between the pH values 7.5 and 8.5, and no action was observable at pH values below 6.0 or above 9.8. For the larger amount of enzyme, complete removal of elastin occurred between the pH values 5.5 and 8.5 and no action was observable at pH values below 3.8 or above 9.8. Both amounts of pancreatin are greater than ordinarily added to a bate liquor, but it must be remembered that the enormous numbers of bacteria always present in bate liquors also produce enzymes.

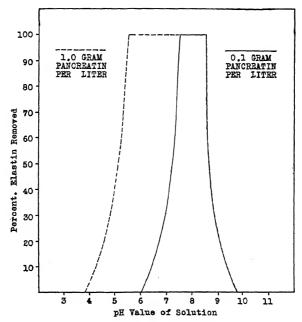


Fig. 152. Percentage Removal of Elastin Fibers from Calf Skin by Pancreatin as a Function of pH Value. Time of digestion, 24 hours. Temperature 40° C.

Similar series of experiments were run to show the effect of time of bating, and the results are shown in Fig. 153.

Complete removal of the elastin fibers by the stronger enzyme solution was effected in from 6 to 8 hours, but 24 hours was required by the weaker enzyme solution. The time required for the first sign of elastin removal, 2 hours for the stronger and 5 hours for the weaker solution, was apparently the time required for the enzyme to diffuse through the grain surface and to make contact with the elastin fibers.

Fig. 154 shows the effect of the amount of enzyme used.

Complete removal of the elastin is effected by 0.1 gram of pancreatin in 24 hours or by 1.1 grams in 5 hours.

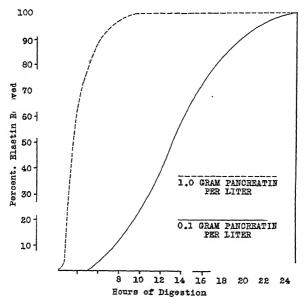


Fig. 153. Percentage Removal of Elastin Fibers from Calf Skin by Pancreatin as a Function of Time of Bating. Temperature 40° C. pH Value 7.6.

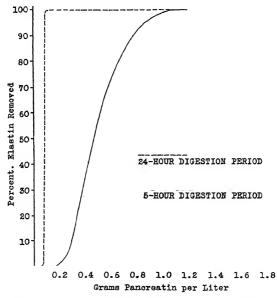


Fig. 154. Percentage Removal of Elastin Fibers from Calf Skin by Pancreatin as a Function of Concentration of Enzyme. Temperature 40° C. pH Value 7.6.

Since many commercial bates contain large percentages of ammonium chloride, Wilson and Daub included a series of tests on the effect of ammonium chloride, the results of which are shown in Fig. 155.

In working with very dilute enzyme solutions, a distinct activating effect was noted upon the addition of 0.5 gram per liter of ammonium chloride, while larger percentages showed an inhibitory effect. With thin calf skin the activating effect was not detectable with the solution containing 0.1 gram per liter of enzyme after a 24-hour digestion period, because all the elastin was removed without adding any ammonium chloride. In order to show the activating effect in these experiments, strips from heavier skins were used, which require a somewhat longer time for complete removal of elastin under fixed conditions. The activating effect of 0.5

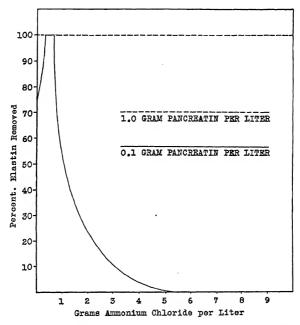


Fig. 155. Effect of Ammonium Chloride upon the Removal of Elastin Fibers from Calf Skin by Pancreatin. Time of Digestion 24 Hours. Temperature 40°C. pH Value, 7.6.

gram of ammonium chloride per liter and the inhibitory effect of greater concentrations are very marked. It is also important to note that the effect of ammonium chloride can be entirely overcome by a sufficient excess of enzyme.

At concentrations greater than 50 grams per liter (about 0.42 lb. per gal.), the ammonium chloride caused a destructive action on the collagen fibers, but, of course, no such concentrations are used practically in bating.

The writer has produced excellent calf leather by removing all the elastin fibers, but he has also produced excellent leather by removing no more elastin than normally occurs in a 90-minute bating period, which is only a small percentage. The removal of all the elastin is always accompanied by a corresponding loss of collagen and the bad effect of this may more than offset the good effects of elastin removal. Some elastin removal probably accompanies all other effects obtained in

bating, but the writer considers it of small importance compared to the very important removal of the degradation products of the epidermal system which would otherwise be precipitated in the grain layer upon pickling or tanning.

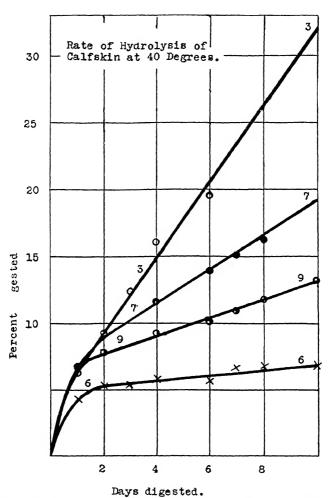


Fig. 156. Effect of Time on the Hydrolysis of Calfskin by Four Different Samples of Trypsin. Temperature 40° C. pH Value 8.0.

Hydrolysis of Collagen Fibers

Although pancreatic enzymes are capable of removing the elastin fibers of skin and the degradation products of the epidermal system before serious damage is done to the collagen fibers, it is important to know that they do act slowly on the collagen fibers and would in time destroy them. The purified enzymes from the pancreas are often called *trypsin*, which is really a mixture of enzymes. The writer has found that trypsin obtained from different reliable concerns differ greatly in their various enzyme activities. Merrill and Fleming studied the

activities of different samples of trypsin on limed calfskin. Fig. 156 shows the rates of hydrolysis of the collagen fibers over a 10-day period, using samples of trypsin from 4 different sources.

These four samples of trypsin had been numbered 3, 6, 7 and 9. No. 9 had by far the greatest action on the collagen fibers, dissolving more than 30 percent of them in 10 days. All 4 enzymes had dissolved more than 5 percent of the collagen in 2 days.

Fig. 157 shows the effect of pH value on the hydrolysis of the collagen fibers of limed calfskin by enzyme No. 6 and also includes hide powder on which the action is much greater because of the greater amount of surface exposed per unit weight of collagen.

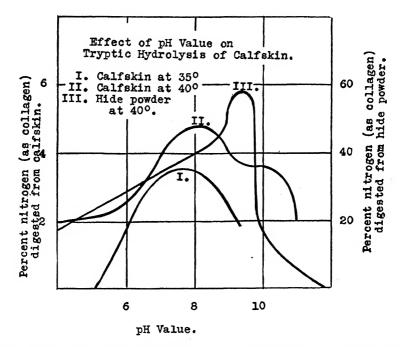


Fig. 157. Effect of pH Value and Temperature on the Hydrolysis of Calfskin and Hide Powder by Trypsin. pH Value 8.0. Time 24 Hours.

The effect on the calfskin is much greater at 40° C. (104° F.) than at 35° C. (95° F.), and the maximum effect occurs at pH values between 7.5 and 8.1. It should be noted from Fig. 157 that the scale for the hide powder is 10 times as great for calfskin, and that the greatest rate of hydrolysis of the hide powder occurs at a pH value above 9. At this point nearly 60 percent of the hide powder was digested in 24 hours.

The effect of temperature on the hydrolysis of hide powder is shown in Fig. 158. As the temperature is raised from 35° to 45° C., a huge increase in hydrolysis of the hide powder occurs. Fig. 158 should be compared with Fig. 118 of Chapter 8 showing the effect of time and temperature in the hydrolysis of calfskin by saturated limewater.

Although the loss of material from the collagen fibers in ordinary bating may be small, it is probably always appreciable and has an effect upon the final character of the leather.

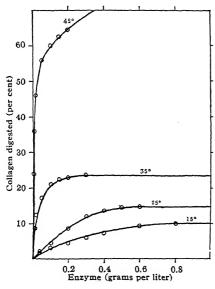


Fig. 158.

Effect of Temperature and Amount of Enzyme on the Hydrolysis of Hide Powder by Trypsin. pH Value 8.0. Time 3 Hours.

Falling

Of the seven important things listed above as occurring during bating, the fourth was falling. When the alkaline swelling or plumping of a skin is reduced by neutralization, the skin becomes increasingly soft and flaccid; this is known as falling. When skins are placed in pure solutions of acids or alkalies, they swell, becoming plump. In acid liquors, without salt, as the pH value is decreased below 5.0, the skins becoming increasingly plump until a pH value of 2.4 is reached, below which they start to fall again. In alkaline liquors, as the pH value is increased, above 7.7, the skins become increasingly plump until a pH value of 12.6 is reached, above which they start to fall again. Wilson and Gallun developed a method of measuring the degree of plumpness of calfskins, and then used it to determine the effect of pH value on plumping (or its reciprocal falling) over the range 4.0 to 11.0. They first measured the thickness of the skin with a Randall & Stickney gauge (see Fig. 202 of Chapter 11) under a standard set of conditions and then repeated the measurement on the same piece of skin after bringing the piece to equilibrium with a solution of fixed pH value. The ratio of the final reading to the initial reading was taken as the measure of the degree of plumping. Their results are shown in Fig. 159.

The pieces of calfskin were placed in solutions of dilute sodium phosphate, each at a different pH value. The sodium phosphate was used to prevent wide variations in pH value and for this reason is known as a buffer. The limed stock is in equilibrium with a solution of pH 12.5. As the pH value is decreased, the skin loses plumpness until it becomes a minimum at a pH value of 7.7. It will be noted from Fig. 159 that there are two points of minimum, one at a pH value of 7.7 and the other at 5.0. At pH values below 5.0 or above 7.7, the skin becomes increasingly plump. These two points represent the points of minimum plumping or of maxi-

mum falling. Wood observed that the pH values of the old dung bate liquors varied from 6.4 to 8.4. Modern bate liquors lie within this same range. One can now appreciate the deep secret of the old bate master. With his highly developed sense of feel, he could pick the point at which maximum falling occurred, which happens to be at a pH value of 7.7 for stock with pH value falling from 12.5. By creating conditions for obtaining the condition of maximum falling, he was actually controlling the pH value at about 7.7, at which point the enzymes are most active, even though he may have had no conception of pH value or of the presence and activity of enzymes.

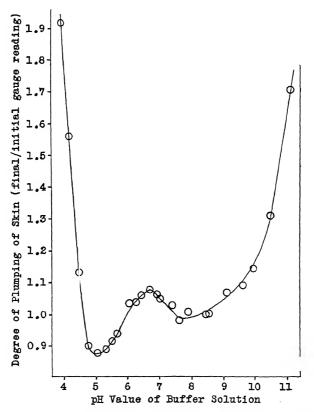


Fig. 159. Degree of Plumping of Calfskin as a Function of pH Value.

The writer made a number of tests of this psychology. In each test, he put a pack of skins into a vat with no enzymes at all and added acid gradually until the stock reached equilibrium with a pH value of 7.7 and the bate master invariably pronounced the stock bated just right. Some bate masters could actually bring the pH value to approximately 7.7 without a pH indicator, simply by feeling the stock until it was "just right." Even though the stock given no enzyme was pronounced just right by the bate master, it made only poor, grainy leather characteristic of unbated stock.

Merrill showed that the rate of falling increases greatly with the temperature. At 95° F., complete falling of calfskin requires from 1 to 2 hours, whereas it is not complete in 17 hours at 45° F.

Regulation of pH Value

Long before the concept of pH value and its importance in tanning was known, the bating operation was successfully bringing the stock to a uniform pH value before it entered the tan liquors. About 80 percent of the bated weight of a pack of skins is due to water or to used bate liquor. Even though the stock is washed with water, it tends to maintain the equilibrium acquired in the bate liquor until it comes into contact with strong liquors. If the equilibrium pH value of the bated stock is variable, difficulty will be experienced when putting it directly into vegetable tan liquors, because the rate of tanning, the rate of diffusion of the tan liquor into the skin, the color value of the tan liquor and its tendency to oxidize are all functions of pH value. Because the pH value during bating must be controlled, it contributes to the pH control of later operations.

Deliming

In using a dung bate, Wood found that the lime content of the stock varies from 3 to 6 percent on the dry weight of the stock before bating and from only 0.5 to 0.9 percent after bating. But his pH measurements showed that some of his bate liquors in use were faintly acid. Many tanners today do not delime their stock before tanning and add no acid to the bate liquors. In such cases, no real deliming occurs during bating. Operating like this years ago, the writer observed that the pH values of the bate liquors dropped only to about 8.4 and that then no deliming occurred, although the caustic lime was converted into calcium carbonate.

Deliming is not truly a function of bating and actually does not occur if the liquors are always alkaline. For effective bating, the writer prefers to delime the stock by the use of acid before bating, but this is certainly not universally practiced, as will be made clear in the discussion of bating stock for making sole leather.

Bacterial Action

Years ago, the writer made a practice of using the same Oropon liquor for bating 8 successive packs of calfskins, strengthening with fresh Oropon for each new pack. He also used to make bacterial counts of the liquors after using each time. A typical series of counts for one liquor after using for 8 successive packs in millions per cubic centimeter of bate liquor, were 93, 370, 590, 920, 1330, 1110, 770, and 630, respectively. A curious point was that the finest leather came from the bate liquors having the highest bacterial counts. It is interesting to note the steady increase in bacterial count with successive packs from 93 million per cc. to more than a billion for the fifth pack and then the continuous decrease in count, suggesting possibly that the maximum rate of bacterial reproduction could not be maintained because of the inhibiting action of the reproduction products.

Many bacteria produce and secrete enzymes in the course of their reproduction, and it is supposed that these enzymes play a large role in bating in practice. The bating action can be obtained satisfactorily by using pancreatic enzymes under sterile conditions; but such conditions are difficult in practical operation and much larger amounts of enzyme are required. The beneficial effects of bacteria are utilized in the procedure given above for calfskins by making up each new bate

liquor with 500 gals, of bate liquor previously used. This procedure also provides greater uniformity of results than when using the same bate liquor for a fixed number of successive packs.

Becker isolated 54 varieties of bacteria from dog dung and studied the actions of many of them upon skin. He found one, which he called *B. erodiens*, capable of producing a falling action of limed skin similar to that of the dung bate itself. An artificial bacterial bate was developed independently by Wood in England and by G. Popp and H. Becker in Germany, but they later joined forces and perfected the artificial bate known as erodin, which consists of a nutrient material to which a pure culture of *B. erodiens* is added before using. This material has been used on a commercial scale and found to be a satisfactory substitute for dung for some kinds of leather.

Since B. erodiens does not secrete tryptic enzymes, Wood has suggested adding to it bacteria obtained from the roots of wool in the sweating process which secrete a mild form of proteolytic ferment. The susceptibility of erodin liquors to become contaminated by foreign bacteria presents an obstacle to any very widespread increase in their use. In using erodin, Wood has observed that the fresh liquor usually has a pH value of about 6.6 and this increases to about 7.3 during the bating operation.

Cruess and Wilson isolated 10 varieties of bacteria from pigeon dung and found that the falling of limed skins could be brought about by pure cultures in dilute skim milk. If the bating operation were unduly prolonged, the skin proteins became hydrolyzed, but they found that danger from this source could be minimized by using a liquor containing 0.5 per cent of glucose. They pointed out that the glucose was decomposed into acids which checked bacterial action and assisted in the removal of lime from the skin.

Like bacteria, many species of molds (Fungi) also secrete enzymes during the course of their reproduction. Jacques Wolf & Co. has developed a commercial bate under the name Fungizyme, which contains as active principle enzymes secreted by certain species of molds. Although the writer has had no personal experience with the use of Fungizyme, he has examined some very satisfactory leather that had been bated with it.

After the successful adoption of Oropon in the manufacture of all types of leather everywhere in the world, healthy competition developed in the manufacture of bating materials, a number of which contain pancreatic enzymes as the essential ingredient. It was natural also that other sources of enzymes should be investi-Being interested in the use of enzymes for the brewing industry, the Wallerstein Co. turned their attention to the leather industry and in 1932 offered tanners a bating material, under the name of Biobate, which contained enzymes of bacterial origin, particularly a proteolytic enzyme obtained from bacillus subtilis mesentericus. This was prepared under United States patents No. 1,227,525 and No. 1,744,742 granted to August Boidin of France and Jean Effront of Belgium. As early as 1925, enzymes from a fungous source were the subject of study by C. J. M. Le Petit of France who obtained U. S. patents No. 1,767,536, No. 1,-772,258 and No. 1,779,243 in 1930; these were acquired prior to their issue by Röhm & Haas Co. Later, Dr. O. Röhm was granted U. S. patents No. 2,139,209, No. 2,157,969 and No. 2,179,899 covering improvements in the application of fungous enzymes to bating.

With the advent of insulin for the treatment of diabetes, it was apparent that the medical profession would eventually require the entire output of pancreatic glands. Studies of enzymes produced during the growth of molds have been in continuous development since 1925. It has been shown that enzymes of fungous origin are just as effective in bating as pancreatic enzymes, and Oropon of fungous origin is now available in quantities sufficient to supply the entire needs of the industry and is actually being used in many tanneries.

Bating Goatskins

Most of the goatskins tanned in this country are imported in the dry state from many parts of the world, and skins from different countries differ widely in their nature. For this reason, no single rigid procedure can be laid down that is satisfactory for all goatskins. Skins of a hard nature usually require more drastic treatment than those of a soft nature. All that we can hope to do here is to describe several procedures for goatskins that are in satisfactory use as a first guide to the tanner. He must then experiment himself to determine the best conditions for each type of skin that he is working. This is really not so difficult as

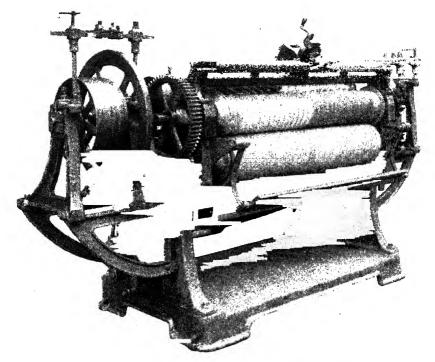


Fig. 160. Evans' Slate Scudding Machine Used for Goatskins after Bating.

it might seem to a layman. The test of à procedure is the final result. As long as the tanner has one rigidly defined procedure from which to make a start, he can run comparative packs, one with the initial procedure and one in which only one factor has been varied. When a change in one factor gives a better result, the change is made in the standard and the experiments continued with the new standard as a basis. In order to get conclusive results, a change in more than one variable must never be made until the result of the change is known. It is not

always necessary to await the final finishing of the leather to get the results, as short cuts can be made like that described for calfskins. The final decision, however, must be made only on the basis of quality of the finished leather.

As a rule, goatskins require more drastic action than calfskins. One method that the writer has found generally successful is to treat the stock according to the procedure for calfskins given above, with the following exceptions:

In the liming operations discussed in Chapter 8, our unit pack of goatskins contained 1600 lbs. dry weight of stock. After liming, unhairing and washing, the weight will vary greatly according to the nature of the stock. For bating, keep the pack at 1600 lbs. original dry weight. Delime as for calfskins, but in bating, use 50 lbs. of Oropon A and a bating time of 3 hours for the softest-natured skins, and increase the amount of Oropon A to 100 lbs. and the bating time to 5 hours for the hardest-natured skins. After hauling the skins from the bate liquor, scud them on a machine of the type shown in Fig. 160. This machine is equipped with spiral slate blades and it operates much like a fleshing machine, but it merely scuds the grain surface of the skins. After scudding, wash the stock in running water at 70° F. in a drum for 30 minutes and then send it on to be pickled or tanned.

Some tanners use essentially the foregoing procedure, but eliminate the deliming operation and the pH control entirely. Although they get apparently satisfactory results, the writer has always obtained a finer quality of leather by deliming and controlling the pH value. Some tanners who do not delime, put the stock into the bate and run the paddle for only 30 minutes and then again for 30 minutes at the close of the day and let the stock stand idle over night. Next morning they run the paddle for 30 minutes and haul out the pack. The initial temperature is 92° F., but it is allowed to drop with no further heating until the stock is hauled out.

Some goatskin tanners who bate their stock over night use two liquors. The stock is dumped first into a liquor used once previously. The paddle is run for 20 minutes while the liquor is being heated to 85° F. The paddle is then stopped and the stock is allowed to stand idle for about 3 hours. It is then transferred to a fresh liquor at 85° F. containing from 4 to 12 oz. of Oropon A per 100 lbs. limed weight of stock. The paddle is run for 20 minutes and then stopped and the stock is allowed to stand idle over night. Next morning the paddle is run and the stock is hauled out, scudded and washed.

Goatskins unhaired by the Arazym process are usually bated over night in a liquor containing from 0.10 to 0.25 percent of Oropon A and 0.25 percent of sodium bicarbonate based on the unhaired weight of the pack, with the temperature at 90° F.

Bating Sheepskins

Most tanners of sheepskins buy their raw stock already dewooled, bated and pickled. Some tanners of sheepskins for glove leathers buy them after dewooling, but before bating or pickling. Others buy imported dry skins with the wool on and soak, dewool and lime them themselves. The stock is first soaked for 1 day in fresh water at 45° to 50° F. and then 1 day in fresh water at 50° to 60° F. Then for a pack of 75 to 85 skins, put into drum and wash for 10 minutes with running water at 100° F. and drain. Add 12 lbs. of soda ash and 3 lbs. of sodium oleate soap in 15 gals. of water at 100° F. and then add 3 gals. of naphtha. Run 15 minutes and dump the stock. Trim and flesh and put stock back into drum. Add 6 lbs. of soda ash and 8 lbs. of sodium oleate soap in 18 gals. of water at 100° F. and run 15 minutes. Then drain and wash in running water at 80° F. for 10 minutes. Then dump the stock and dewool with lime-sulfide paste, as described in Chapter 8. Then

lime the stock in pure limewater, containing a considerable excess of undissolved lime, in a paddle vat at 70° F. for from 6 to 12 days, running the paddle for 2 minutes each morning and evening. The stock is then scudded, fleshed and washed in running water at 70° F. for 40 minutes.

Stock received directly after dewooling can be put directly into the limewater and the process continued from there. The stock is then put into a paddle vat for bating. For a pack of 5000 lbs. limed weight, put 1900 gals. of water at 105° F. into the paddle vat of 2500 gals. capacity, dump the stock into the water and run the paddle continuously. Add 75 lbs. of Oropon A and raise the temperature to 100° F. The writer prefers deliming the stock in the paddle before bating, as for calfskins. If this is not done, add dilute sulfuric acid cautiously during bating so as to maintain as nearly as possible a pH value of 7.4, making frequent measurements of pH value with the phenol red comparator. When following this procedure for the first time, take the stock out after bating for 90 minutes, but in running subsequent tests run comparative packs for longer periods of time and note whether or not improvements are obtained. After bating, wash the stock in running water at 70° F. in a drum for 2 minutes and send to be pickled or tanned.

In attempting to subject sheepskins to procedures developed for other types of stock, serious consideration should be given to the contrasting structures of sheep skins as compared to those of the other types of stock. Fig. 28 of Chapter 1 shows the structure of a domestic sheep skin. A very much larger proportion of the thermostat layer (grain layer) consists of fat glands and sweat glands than for almost any other type of skin, and the hair follicles are not straight, but sharply curved. The reticular layer is of very loose structure and is not joined as securely to the grain layer as with other types of skins. Fig. 150 shows the peculiar arrangements of the elastin fibers, which cause the grain surface to become rough. There appears to be little doubt that at least a partial breakdown of the elastin fibers is essential to make very smooth sheepskin leather. The abundance of glands in the thermostat layer provides more degradation products for removal by bating than is the case for other types of skins. More drastic bating is thus required; but it must be remembered that sheep skins have a very loose structure and cannot withstand mechanical handling as well as other types.

Bating Hogskins

Many tanners do not bate hogskins because they have a naturally rough grain surface and the entire thickness left after fleshing and unhairing is thermostat layer alone; the reticular layer consists entirely of adipose tissue, as shown in Fig. 33 of Chapter 1. Fig. 151 shows the sparse distribution of elastin fibers in hogskin. However, the writer has obtained great improvements in hogskin leathers by bating them exactly as described above for calfskins, except for doubling the amount of Oropon used.

Bating Various Other Types of Stock

Kangaroo skins and various types of dry skins can be bated satisfactorily according to the procedures given for goatskins; in most cases, only minor adjustments may be required. Practically all stock for shoe uppers can be bated exactly according to the procedure given for calfskins, with possibly minor adjustments which the tanner must work out for himself. The same could be said of heavy hides for sole leather, harness leather and other heavy leathers were it not for the fact that the tanning procedures of perhaps a majority of heavy-leather tanners are based on raw stock entering the tan liquors still much plumped by lime. Many tanners of vege-

table-tanned sole leather maintain pH values of their tan liquors low enough to take care of a large percentage of lime carried in by the stock. In such tanneries, if the steer hides were delimed and bated according to the calfskin procedure, they would contain so little alkali that the acid tan liquors would cause an acid-swelling of the hides after being in the liquors for a few days, and the stock would be ruined. A vegetable-tan yard must be adjusted to receive the stock normally coming from the beamhouse. If the condition of the stock from the beamhouse is changed without simultaneously making adjustments in the tan yard, the results may be disastrous.

Bating Steer Hides for Sole Leather

Some sole leather tanners do not bate their stock at all. After the stock has been unhaired, fleshed and scudded, it is washed in a drum with running water at 70° F. for 15 minutes. The hides are then suspended in a rocker vat, like that used in tanning, containing only cold, running water, and left there for 24 hours. They are then hung over into the first rocker vat for tanning, which will be described in Chapter 20. Although the tan liquor is acid in reaction, the interior of each hide is still strongly alkaline with lime. In the course of the tanning, the lime from the hides would gradually neutralize all the acid in the tan liquors and poor tanning results would be obtained, if there were no continuous source of acid to take care of the lime in the hides.

The tanner provides a continuous source of acid in his tan liquors by using in his tanning mixture such tanning materials as myrobalans, which ferment readily with formation of acetic and other organic acids. He controls the percentage of acid formed by periodic measurements of the pH values of the tan liquors. Having determined by experience the range of pH values that best serves his purpose, he maintains this range by regulating the amount of myrobalans used. If the pH values rise above his standard values, he increases the proportion of myrobalans added to the liquors; if the pH values fall below the standard values, he decreases The pH values accepted as standard are those that produce neutralization of the hides at any one time only to the depth that the tannins have penetrated in that This method produces the very plump leather that sole-leather tanners desire, and it takes a very long time to bring a tan yard operated on this basis into a state of balance. If a single pack of hides were completely delimed and then put through such a yard, the acids would penetrate the hides very much more rapidly than the tannins, and the hides would be destroyed by an acid swelling. Completely delimed hides can safely be put through a yard only when the pH values of the liquors are high enough to prevent an undue acid swelling of the untanned layers of the hides.

Failure to bate the hides results in leather that does not have a fine grain, and protein degradation products in the grain layer combine with tannin to retard greatly the penetration of tannin through the grain surface. As bating hides for sole leather is very beneficial, sole-leather tanners in increasing numbers are now bating their stock. The universal bating of sole leather has been retarded not by any lack of desire to bate, but by lack of knowledge as to just what to do so as not to upset the delicate balance of the tan yard that would mean disaster to some tanners.

Sole-leather tanneries may be divided rather sharply into two classes: those whose liquors are balanced at lower pH values for stock containing much lime, and those whose liquors are balanced at higher pH values for stock containing much less lime. This chapter is not the place to argue the advantages and disadvantages

of the two classes of tanneries. It is desirable to bate all raw stock, and methods have been developed for both classes.

Bating for Yards of Lower pH Value

For tan yards of low pH value, the stock must not be delimed. The practical value of bating is limited to the grain layer which represents less than one-fifth of the total thickness of the wet hide. After the stock has been washed with slowly running cold water in a rocker vat over night, as described above, drain off the water and refill the vat with water at 100° F. containing ½ percent of Oropon XX based on the limed weight of the stock, and enough sulfuric acid to give the liquor a pH value of 5.0. The temperature of the water should really be such as to make the temperature of the liquor after contact with the cold stock about 90° F. Allow the stock to rock in this liquor for 2 hours; then drain off the liquor, replace by cold, running water, and allow to wash for 1 hour. Then start the stock through the tan liquors. The conditions described are to be taken merely for purposes of making a practical start, after which the time, temperature and percentage of Oropon can be adjusted by experiment to give the best results. Although the stock



Fig. 161.

A Salometer.

Courtesy Taylor Instrument Companies

will still contain the bulk of its lime, some deliming will take place; the tanner must therefore be on the alert to adjust the pH values of his tan liquors, if that should prove to be necessary. As against no enzyme bating, the stock will show a marked improvement in fineness of grain and clearer color and the tannins will penetrate more rapidly through the grain surface; but the final adjustments must be made by the tanner himself after careful experimenting to determine the best conditions for his own particular stock.

Bating for Yards of Higher pH Value

If the pH value of the tail liquor is usually about 5.0 and the pH value decreases very gradually toward the head liquor to a low of about 3.5, bating can be done much more effectively in a paddle vat. No myrobalans or other markedly acid-producing materials are used in the tan liquors, wherein the pH values may be lowered when necessary by direct addition of acid. As a start, follow the procedure of deliming and bating given above for calfskins, but limit the time of bating to 30 minutes. With this as a standard, run comparative tests to determine the ideal procedures for the conditions of the tannery.

Pickling

Many types of stock are tanned directly after bating and rinsing, but certain other types, particularly for chrome-tanned leathers, are pickled before tanning. Pickling consists of bringing the bated stock to a condition of equilibrium in a bath of sulfuric acid and salt of fixed concentrations. It has the enormous advantage of bringing stock of all kinds and conditions into a uniform state. The procedure will be described for a pack of 5000 lbs. of bated calfskins, but it is essentially the same for all types of stock.

Dissolve 2500 lbs. of salt (sodium chloride) in water to make a total volume of 1900 gals. of brine at 60° F. in a 2500-gal. paddle vat, and add 95 lbs. of concentrated sulfuric acid (66° Baumé). Mix well, start the paddle running and dump the 5000 lbs. of bated calfskins into the liquor. After running for 1 hour, take a sample of the pickle liquor for analysis.

A tanner should have the assistance of a chemist when making his first determinations of the salt and acid contents of the pickle liquor, and should get a reliable source of the standard solution and equipment he will need. But anyone can learn very quickly how to make the determinations without further assistance from a chemist. He will need a burette, preferably of the automatic type, calibrated in tenths of a cc.; a 25-cc. pipette for measuring off the pickle liquor; a 50-cc. Erlenmeyer flask; a supply of "tenth-normal sodium hydroxide" and of methyl orange indicator solution; and a tall glass cylinder of about 250 cc. capacity. He should also refer to Wilson and Merrill's book "Analysis of Leather and Materials Used in Making It," 338-9. He should also have a salometer or other hydrometer for measuring specific gravity. A salometer is shown in Fig. 161.

Table 22. Lbs. of Salt per 2500 Gals. of Pickle Liquor as Determined by Salometer Reading at 60° F.

Specific gravity	Lbs. salt per gal. liquor	Lbs. salt per 2500 gals. liquor
1.0659	0.800	2000
1.0678	0.825	2063
1.0696	0.845	2113
1.0715	0.867	2168
1.0733	0.890	2225
1.0759	0.924	2310
1.0785	0.958	2395
1.0810	0.990	2475
1.0829	1.013	2533
1.0848	1.040	2600
1.0867	1.065	2663
1.0886	1.090	2725
1.0905	1.118	2795
1.0924	1.140	2850
1.0943	1.167	2918
1.0962	1.190	2975
	Specific gravity 1.0659 1.0678 1.0696 1.0715 1.0733 1.0759 1.0785 1.0810 1.0829 1.0848 1.0867 1.0886 1.0905 1.0905	gravity gal. liquor 1.0659 0.800 1.0678 0.825 1.0696 0.845 1.0715 0.867 1.0733 0.890 1.0759 0.924 1.0785 0.958 1.0810 0.990 1.0829 1.013 1.0848 1.040 1.0867 1.065 1.0886 1.090 1.0905 1.118 1.0924 1.140 1.0943 1.167

In order to determine the amount of *salt* left in the paddle vat, fill the 250-cc. glass cylinder to the brim with the pickle liquor, insert the salometer and note the reading at 60° F. From Table 22, read off the number of lbs. of salt per 2500 gals. of liquor corresponding to the salometer reading.

If the salometer reading is 40 or higher, do not add any more salt; if it is lower than 40, subtract the amount of salt shown in the table from 2500 lbs. and add the difference to the paddle vat. If the paddle vat has a capacity including the skins of some amount different from 2500 gals., get the amount of salt by taking the amount of salt given in the table for 1 gal. and multiply it by the total volume in the vat. Then add the salt necessary to make a total of 1 lb. per gal. If no salometer is available, use any method for determining specific gravity and use the specific-gravity column in the table to find the amount of salt present. A barkometer reading to 100° can be used. Divide the barkometer reading by 1000 and add 1. This will give the specific gravity, from which the amount of salt can be read from the table. For example, if the pickle liquor has a barkometer reading of 81°, divide 81 by 1000 to get 0.081 and add 1 to get 1.081 for specific gravity. This corresponds to 2475 lbs. of salt.

It is the sole object of this salt control to have the final pickle liquor, when the stock is ready to be hauled out, contain 1 lb. of salt for each gal. of liquor plus skins.

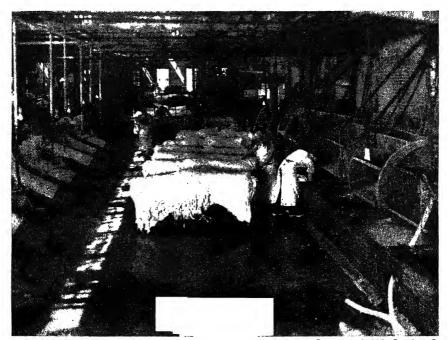
In order to determine the amount of acid left in the paddle vat, pipette 25 cc. of the pickle liquor into the 50-cc. Erlenmeyer flask and add one drop of the methyl orange indicator, which will cause the liquor to turn red in color, if there is any acid left. If it turns red, fill the burette to the 0.0 mark with standard tenth-normal sodium hydroxide and then run it drop by drop into the 25 cc. of pickle liquor in the flask, twirling or shaking after each addition, until the color just starts changing from red to yellow and is of an orange shade. Note by reading the burette how much of the standard solution was required to change the color in 25 cc. of the pickle liquor. If the reading is 6.0 or more, add no more acid at this time. A reading of exactly 6.0 means that the vat contains 25 lbs. of pure acid. Thus each 1.0 cc represents $4\frac{1}{6}$ lbs. of acid in the 2500-gal. vat. Subtract the reading from 6.0 and multiply the difference by $4\frac{1}{6}$ and the result will be the number of pounds of sulfuric acid to add to the vat. If the pickle liquor turned yellow without the addition of any standard alkali, add 25 lbs. of acid to the vat.

After the paddle has run 2 hours, again determine the amounts of salt and acid and add whatever may be necessary to bring the amount of salt to 2500 lbs. and the amount of acid to 25 lbs. For vats of any other size, the amounts to maintain are 1 lb. of salt. and 0.01 lb. of sulfuric acid per gal. of liquor plus stock. Leave the stock in the liquor over night, having the paddle run for about 1 minute each hour, if possible. Next morning, run the paddle for 30 minutes, take a sample and repeat the determinations of acid and salt and add whatever may be necessary to make the final concentrations of 1 lb. of salt and 0.01 lb. of acid per gal. Then haul out the stock and pile it on wooden horses or on a flat truck.

Each liquor may safely be used to pickle 15 packs of skins before running it to the sewer. For each succeeding pack, add water to make a total of 1900 gals, before the stock is entered and add 600 lbs, of salt and 70 lbs, of acid. Mix well, dump in the pack of 5000 lbs, of bated stock and proceed exactly as for the first pack. Always run the paddle for at least two hours after the stock is entered and always pickle over night, running the paddle for 1 minute out of each hour after the first two hours. Regardless of the size of the pack or capacity of the paddle vat, always add salt and acid in such amounts that the final liquor, just before hauling out the pack, contains 1 lb. of salt and 0.01 lb. of acid per gal.

The 66° Baumé sulfuric acid really contains only about 93 percent by weight of sulfuric acid, but this makes no practical difference so long as the final testing of the liquor shows a titration of 6.0 cc. for 25 cc. of pickle liquor. In the older liquors, the salometer reading will include accumulated lime salts, but this also makes no practical difference; the important thing is to have a final salometer reading of 40.

The same procedure may be used for any type of bated stock without any change. In pickling sheepskins for storage, it is customary to increase the final amount of acid in the liquor about six-fold, but this is done only to prevent mold growth



Courtesy of Ohio Leather Co.

Fig. 162. Hauling Out and Horsing Pickled Calfskins.

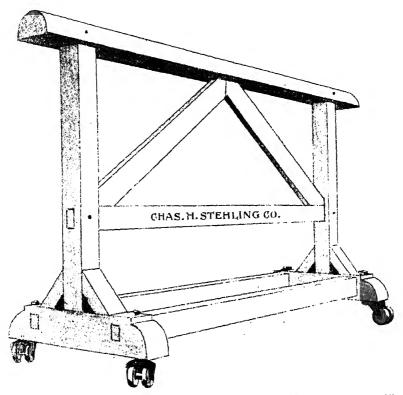
and is not necessary when the stock is to be tanned in a reasonable length of time. In a cool place (about 60°F.) pickled stock may be kept for many months without harm; but it is desirable to repickle it, doubling the final amount of acid, whenever it has been piled for a week or longer after pickling. This is merely to equalize any irregularities in distribution of acid before the stock enters the tan liquors.

Fig. 162 shows workmen hauling calfskins from paddle vats and piling them on wooden horses to drain. Fig. 163 shows a typical wooden horse.

It is customary to pickle all stock to be chrome-tanned by the one-bath process. Some tanners of vegetable-tanned leathers assort the stock after bating and send to be pickled only the stock that is salt-stained or discolored by iron stains. In vegetable-tanning pickled stock, special precautions must be taken to have a sufficient amount of salt present in the tan liquors to guard against acid swelling.

Drenching

Some tanners do not pickle their stock, but subject it to a treatment known as drenching to give it a mildly acid reaction before tanning. The drench liquor is prepared by soaking bran in water in the proportion of from 4 to 8 lbs. of bran per 100 gals. of water at about 90° F. and allowing it to ferment, with formation of organic acids. The skins are treated with this liquor in a paddle vat, and skilled workmen determine by the feel and appearance of the stock just how long



Courtesy Chas. 11. Stehling Co.

Fig. 163. A Typical Wooden Horse for Piling Wet Stock.

to carry on the drenching for the particular tanning process to be employed. This may vary from one to several hours. The organic acids dissolve any lime remaining in the stock and the particles of bran exert a cleansing action on the skins, absorbing dirt and greases. However, in some tanneries, fermentation is carried out in special tanks and only the clear, decanted acid solution is used on the stock.

During the drenching operation, a considerable amount of gas is evolved, which causes the skins to float to the surface when the paddle is not running. In a drench in actual use, Wood analyzed both the gases and the acids formed and found them to have the following approximate percentages:

Gases		Acids			
Hydrogen Nitrogen Carbon dioxide Oxygen Hydrogen sulfide	47 26 25 2	Lactic Acetic Formic Butyric	77 19 3 1		

It was found that the starch of the bran is converted into glucoses and dextrin by the action of an amylolytic enzyme, cerealin, discovered by Mege Mouries. It resembles the diastase of translocation described by Brown and Morris in their work on the germination of grass seeds. It transforms starch into dextrin and glucose, whereas ordinary malt diastase transforms starch into dextrin and maltose. The action of cerealin is much slower than that of diastase. The sugars are then fermented by bacteria (Bacillus furfuris) with the formation of the organic acids listed above. The principal acid produced is lactic; the acetic acid is produced directly from the glucoses without any preliminary alcoholic fermentation by yeasts.

In the hands of experienced operators, the drenching process seldom gives much trouble, but it is not quite foolproof. If the acidity of the liquor increases rapidly and the skins are not removed in time, they become excessively swollen and may even be destroyed by hydrolysis, especially if the liquor is very warm. How much enzymes play a part in this hydrolysis is not yet known. Apparently danger from this source can be prevented by adding salt to the liquor to repress the swelling of the skin just as soon as it becomes very noticeable.

J. S. Rogers studied the effect of lactic and acetic acids upon the plumping of hide substance and found a maximum degree of plumping at a pH value of 2.3, whichever acid was used. The acid plumping was decreased by addition of tannin.

In his review of the damage to skins that may be caused by improper control of the drenching operation, Wood points out that the discovery of the effectiveness of salt in preventing the destruction of skin in an acid liquor that would otherwise cause excessive swelling represents the origin of the modern pickling process.

Sometimes the fermentation may not proceed in the usual manner and the liquor, instead of becoming acid, turns slightly alkaline, frequently becoming bluish black, due to the presence of chromogenic bacteria. Under these conditions the skin is rapidly attacked by proteolytic organisms, but may be saved if transferred in time to a solution of acid and salt.

When the fermentation is accompanied by a very rapid evolution of gas, the skins may be damaged by the formation of gases inside of the skin; these burst out through the grain surface, leaving small holes. A damage very similar in appearance may be caused by proteolytic bacteria developing on the grain surface, each colony forming a small hole. This usually results from operating the drench at too high a temperature. A high temperature, especially in the presence of an excess of acid over that normally present, may result in a considerable amount of hydrolysis of collagen, and leather will feel rather spongy and empty.

When bacteria attack the grain during drenching, the surface of the finished leather may show dull patches, as though it were etched. In one instance, Eitner found that this was caused by *Bacillus mcgaterium*, which formed a slimy film over the grain surface, which was attacked by a proteolytic enzyme secreted by the bacillus.

Wood and Wilcox showed that if the acids ordinarily found in the drench are used in pure solution in the proportions in which they occur in the drench, the action upon the skin is the same, except for being more rapid. With the appreci-

ation of the fact that the active constituent of the drench is the acid formed, tanners began to substitute pure solutions of organic acids, such as lactic and acetic. These could be used with safety, simply by adding the acid at such rate as to keep the solution just neutral to methyl orange. Hydrochloric acid, being cheaper, is often used, although it makes the control more delicate. In this way practically all the lime can be removed from the skins and the skins then combine with a sufficient amount of the acid so that they do not reduce the acidity of the ordinary vegetable tan liquor into which they may be put.

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Chapter 10

Vegetable-Tanning Materials and Their Properties

If a wet, raw skin is thrown over the limb of a tree or across a log, it usually becomes stained. The stained areas appear quite different from the areas not stained, both while the skin is still wet and after it has dried. If the skin is allowed to decompose, it will be found that the stained areas do not putrefy. This fact was certainly known more than 12,000 years ago and probably was discovered not long after humans began to kill animals and flay them to get their skins for protective coverings. Practically every archeological discovery of ancient civilizations has yielded treasures in the form of leather goods. Discoveries of civilizations dating back into the early stone age have yielded stone daggers encased in well made leather sheaths.

Ancient Leathers

A famous German archeologist, Dr. Walter von Stockar of Berlin, found many remains of ancient civilizations in northern Germany dating back to 10,000 B. C. In all of them, he found leather goods in the forms of sheaths, straps, trimmings, etc. He kindly sent the writer some nine tiny samples dating from 2300 B. C. to 400 A. D. In a tiny piece of leather strap, dating from 2300 B. C., the writer found the fibers still quite strong and in good state of preservation. All the ancient specimens of leather goods are so highly treasured that the writer could not hope to get enough of any one to make a complete analysis and thorough study. However, he secured enough of a sample of leather dating back to 50 B. C. to get a good photomicrograph of it. A vertical section of it is shown in Fig. 164 at a magnification of 120 diameters. The entire grain layer has been worn away, but the size and arrangement of the fibers suggest that it may have been made from a young animal of the ox family. It has been vegetable-tanned and the fibers are still strong and flexible.

All of Dr. von Stockar's findings prove that vegetable tanning was a highly developed art over 12,000 years ago.

It has been known for thousands of years that most forms of plant life contain an active principle, capable of extraction by hot water, that is capable of combining with protein, converting it into the imputrescible material known as leather; but only during the last hundred years have chemists developed the technic required to determine the chemical nature of this active principle, which consists of thousands of related chemical substances classed under the general name of the tannins. In 1913, Emil Fischer announced his success in synthesizing the first tannin produced artificially. It was the chemical substance known as penta-meta-digalloyl-beta-glucose, which is allied to the tannins found in Chinese nutgalls.

Spurred on by Fischer's success, chemists have since made very extensive studies of the tannins. Much of this work is still primarily of academic interest, because the natural tannins are abundant and cheap, and it is unlikely that any synthetic tannin could compete with the natural tannins in price during our time.

Commercial Sources of the Tannins

Among the materials which have assumed commercial importance as a source of tannin for leather manufacture are barks, woods, leaves, twigs, fruits, pods, and roots. Tanning extracts obtained from different sources show very different properties, which are due in a large measure to the foreign matter extracted with the tannin. Certain plant cells are very rich in tannin. In the living cell, the tannin occurs dissolved in the cell sap and associated with other substances, including carbohydrates and salts. Lloyd has indicated evidence that the carbohydrates are able to link up with the tannin in some way so as to prevent its attack upon the living protoplasm. The tannin appears to be useful in some way in the metabolism of the plant.



Courtesy Dr. Walter von Stockar.

Fig. 164. Vertical Section of Ancient Vegetable-tanned Leather (about 50 B. C.).

Location: not known.

Thickness of section: 20 microns, or 0.00079 inch.

Magnification: 120 diameters.

Wilson and Thomas compiled for inclusion in "International Critical Tables" a list of natural sources of tannin, arranged alphabetically according to botanical name. This list is given in Table 23. The names and tannin contents were taken from the literature at large for what they may be worth; in some cases the information given may be considerably in error. The place grown may indicate either the place where the sample analyzed was grown or the place where the material grows

Table 23. Sources and Tannin Contents of Different Tanning Materials.

Table 23. Source	es and Tannin Conte	nts of Different Tai	nning Materials.
Botanical Name	Common Name	Place Grown	Per cent Tannin
Abies alba Abies canadensis Abies dumosa Abies excelsa Abies prandis Abies pectinata Acacia acuminata Acacia anema Acacia angica Acacia arabica	White spruce Hemlock fir Hemlock spruce Norway spruce Lowland fir Silver fir Raspberry jam wood Mulga Angica Babul	Northern America Northern America Northern Europe California Europe Australia New South Wales Brazil	Bark 7-13 Bark 8-15 Bark 10 Bark 7-13 Bark 9 Bark 6-15 Bark 4-15 Bark 4-15 Bark 20-25 { Bark 12-20 { Pods 20-42
Acacia binervata Acacia brachybotyra Acacia catechu	Black wattle Blue bush Cutch	Australia New South Wales India	Bark 27-30 Bark 21 Wood ext. 60
Acacia cavenia	Espinillo	South America	Pods 18-21 Bark 6
Acacia cebil	Red cebil	Argentina	Bark 10-15 Leaves 6-7
Acacia cunninghamii Acacia curnpi Acacia dealbata Acacia decora Acacia decorrens Acacia elata Acacia falcata Acacia flavescens Acacia granulosa Acacia horrida Acacia koa Acacia koa Acacia koa Acacia leptocarpa	Pea wattle Curupy Silver wattle Blue bush Green wattle Mountain hickory Stunted wattle Red wattle Yarran Doornbosch Koa tree	Queensland South America Australia, Africa and A New South Wales Australia New South Wales Queensland Queensland New Caledonia New South Wales Cape Good Hope Hawaii Queensland	Bark 9-18 Bark 18 Bark 14-32 Bark 18-51 Bark 18-51 Bark 20-31 Bark 13-37 Bark 19-22 Bark 12 Bark 9 Bark 8-18 Bark 18
Acacia longifolia	Wild willow	Queensland Cyprus and Australia	Bark 7-19
Acacia melanoxylon	Blackwood	New South Wales	Bark 11-13 Leaves 3
Acacia microbotyra Acacia mollissima	Manna wattle	Australia	{ Bark 18-27 Leaves and twigs 20
Acacia neriifolia Acacia oswaldi Acacia pennincrvis	Green wattle Black wattle Miljie Hickory wattle Silver-leaved wattle	Australia Australia Australia Europe and Australia Queensland Queensland Australia	Bark 12-47 Bark 14 Bark 10 Bark 14-38 Bark 8-21 Bark 18
Acacia saligna Acacia sentis	Weeping willow	Australia Australia New South Wales New South Wales Sudan Sudan	Bark 18 Bark 26-50 Bark 6-20 Bark 28 Bark 6-18 Bark 18
Acacia spiralis Accr campbellii Accr campestre Alchornea triplinervia	Guaiac Himalayan maple Field maple	Somaliland New Caledonia India Europe Paraguay	Bark 24 Bark 17 Bark 3 Bark 4 Bark 12 Bark 10 Fruits 25 Bark 16-20
Allophylus edulis Alnus firma Alnus glutinosa Alnus incana Alnus maritima Alnus oregona	Koku Minibari Alder Grey alder Hannoki Red alder	Paraguay Paraguay Japan Europe Europe Japan Pacific states	Bark 10 Fruits 25 Bark 16-20 Bark 10 Fruits 25 Bark 9
Anacardium occidentale Angophora intermedia	Kashew nut	India	Bark 9
Angophora lanceolata	Rough-barked apple	New South Wales	{ Bark 4-5 Kino 65 Bark 6-11
Anogeissus acuminata	Smooth-barked apple You	Australia India	{ Bark 6-11 Kino 61-68 Bark 10
Anogeissus latifolia	Dhawa	India	Bark 16 Leaves 10-18 Shoots 20-30
Anogeissus pendula Apulcia praecox Arctostaphylos uva-ursi Aspidiosperma polyneuron	Yhvihra-pere Bearberry Betelnut palm Palo rosa	India Paraguay Russia India Paraguay	Red tips 54 Bark 9 Bark 11 Leaves and twigs 14 Fruits 10-15 Bark 3
Aspidiosperma quebracho-blanco	White quebracho	Argentina	Leaves 27-28 Bark 4
Avicennia officinalis Banksia integrifolia Banksia serrata	White mangrove Coast honeysuckle Heath honeysuckle	Queensland Queensland Australia	Wood 3 Bark 4-24 Bark 6-11 Bark 11-23

Table 23—(Continued)

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Botanical Name	Common Name	Place Grown	Per cent Tannin
Bauhinia vahlii Betula alba Betula lenta Bostvellia serrata Bruguiera gymnorrhiza Bruguiera parviflora Bruguiera rheedii	Muhurain bark White birch Black birch Salai bark Black mangrove Hagalay Red mangrove	India Northern Europe Northern America India East Africa and Austr Philippines Queensland	Bark 9 Bark 2-18 Bark 3-18 Bark 13 aliaBark 22-52 Bark 7-13 Bark 15-22 Bark 27-42
Bruguiera rhumphii	Mangrove	New Caledonia	Root bark 6 Root wood 9
Bumelia obtusifolia Byrsonima cydoniaefolia Byrsonima spicata Cabralea sp. Caesalpinia brevifolia Caesalpinia cacolaco Caesalpinia coriaria Caesalpinia digyna	Pihkasurembiu Mureci Tamwood Cancharana Algarobilla Cascalote Divi-divi Tari	Paraguay Bolivia South America Paraguay Chile Mexico Çentral America India and Burma	Bark 8 Bark 20 Bark 44 Bark 5 Pods 43-67 Pods 40-55 Pods 30-50 Pod cases 40-60
Caesalpinia melanocarpa	Guyacan	Argentina	{Wood 8
Caesalpinia tinctoria Callitris calcarata Callitris glauca Camellia thea Carapa moluccensis Carissa spinarum Cassia auriculata	Celavinia Black cypress pine Cypress pine Tea Orange mangrove Tarwar	Central America Australia Australia Asia and Africa Queensland India India	Pods 15-23 Wwod 8 Pods 30-32 Bark 12-34 Bark 11-24 Leaves 5-10 Bark 23-34 Leaves 8-12 Bark 16-22 Bark 11-15
Cassia fistula	Amaltas	South India	[Pod husk 17
Castanca cesua	Spanish chestnut	Southern Europe Southern U. S.	Bark 6-8 Wood 7-11 Stump and trunk bark 13 Stump heartwood, center 9 intermediate 13
Castane a denta ta	American chestnut	Southeastern U. S.	edge 16 Root wood 17 Root bark 31 Trunk heartwood, center 9 edge 15
Castanea pubinervis	Japanese chestnut	Japan	{Bark 6 Wood 7
Castanopsis chrysophylla Castanopsis sinensis Casuarina Casuarina equisetifolia Casuarina glauca Ceanothus velutina Ceriops candolleana	Western chinquapin Gie-gay Ironwood Casagha pine Bull oak Snow bush Bahau or mangrove	Pacific states Indo-China New Caledonia Southern Asia New South Wales Western U. S. Australia, India and	Bark 8 Bark 12 Bark 10 Bark 11-18 Bark 12-15 Leaves 17 Bark 24-42
Ceriops roxburghiana Ceriops tagal Cleistanthus collinus	Goran Tangal Kodarsi	Africa India Philippines	Bark 13 Bark 24-37 Bark 33
Ciessaninis collinis Coros romanzofiana Copaifera lansdorfii Coriaria myrtifolia Coriaria nepalensis Coriaria ruscifolia Corylus avellana Coulteria tinctoria	Kodarsi Pindo Kupaih French sumae Tutu Hazel Tara	Paraguay Paraguay France India New Zealand Europe Algeria and Peru	Bark 7 Bark 17 Leaves 15 Leaves 20 Bark 16-17 Bark 5 Pods 43-51
Crossostylis multiflora	Bush mangrove	New Caledonia	{Wood 21 {Bark 3
Cryptomeria japonica Cupania sp. Cupania uraguensis Cupania vernalis Dalbergia sp. Dioscorea atropurpurca Elacocarpus grandis Elephantorrhiza burchellii Enterolobium timbouva Eremophila longifolia	Japanese cedar Cedrillo Kambuata Yaguarataih Yhsapih-ih Cu-nao Blue fig bark Elephant roots Timbo Emu bush	Japan Paraguay Paraguay Paraguay Paraguay Indo-China New South Wales Africa Paraguay New South Wales	Bark 6 Bark 16 Bark 18 Bark 15 Bark 6 Tubers 20 Bark 10 Root 6-22 Bark 22 Bark 22 Bark 5 Leaves 10
Eucalyptus accedens	Spotted gum	Australia	Bark 18
Eucalyptus alba Eucalyptus amygdalina Eucalyptus campaspe	Mountain gum Ribbon gum Silver-topped gimlet	Australia New South Wales Australia	Bark 30-32 Kino 58-65 Bark 27

Table 23—(Continued)

Botanical Name	Common Name	Place Grown	Per cent Tannin
Dotameat Ivalite	Common wante	Trace Grown	(Kino 63-69
Eucalyptus corymbosa	Bloodwood	New South Wales	Leaves 18 Bark 6
Eucalyptus corynocalyx Eucalyptus diversicolor	Sugar gum Karri	Australia Australia	Bark 21-28 Bark 16-20
Eucalyptus erythronema Eucalyptus falcata	White mallet Silver mallet	Australia Australia	Bark 30 Bark 5-32
Eucalyptus gardneri Eucalyptus globulus	Blue-leaved mallet	Australia	Bark 23-31
Eucalyptus gunnii	Eucalyptus Red gum	Australia New South Wales	Sap 28 Leaves 17
Eucalyptus longifolia	Woolly-butt	Australia	\ Bark 11 Bark 2-16
Eucalyptus loxophleba	York gum .	Australia	Bark 2-16 Bark 5-10 Kino 37-45
Eucalyptus maculata	Spotted gum	New South Wales	Bark 3-10 Leaves 5
Eucalyptus obliqua	Stringy bark	New South Wales	Bark 2-17
Eucalyptus occidentalis Eucalyptus occidentalis	Black mallet Red mallet	Australia Australia	Bark 20-26 Bark 34-57
astringens Eucalyptus odorata	White box	New South Wales	Leaves 7
Eucalyptus pallidifolia	Micum	Australia	Bark 28 (Bark 8-30)
Eucalyptus paniculata	Grey ironbark	Australia	{ Bark 8-30 { Kino 72-83 } Kino 32-62
Eucalyptus piperita	Messmate	New South Wales	Leaves 13
Eucalyptus platypus Eucalyptus redunca	Round leaf moort Wandoo	Australia Australia	Bark 25-29 Bark 16-20
Eucalyptus redunca oxymitra	Blue leaf mallet	Australia	Bark 22-30
Eucalyptus resinifera	Stringybark	Australia	{ Bark 1-6 Kino 74
Eucalyptus robusta	Mahogany	Florida	Leaves 12-17 (Bark 16
Eucalyptus rostrata	Red gum	Australia	Kino 30-83 Wood 2-14
Eucalyptus salmonophloia Eucalyptus salubris	Salmon gum Gimlet	Australia Australia	Bark 8-20 Bark 16-19
Eucalyptus siderophloia	Red iron bark	New South Wales	Kino 35-73 Bark 7-13 Leaves 6
Eucalyptus sideroxylon	Ironbark	New South Wales	{ Bark 16-33 Kino 44
Eucalyptus sieberiana Eucalyptus smithii Eucalyptus spathulata	Mountain ash Gully ash Swamp gimlet	New South Wales New South Wales	Bark 5-37 Bark 21-28 Bark 26
Eucalyptus stellulata	Swamp gimlet Black gum	Australia New South Wales	C Barle 13
Eucalyptus stuartiana	Apple	New South Wales	Leaves 17 { Bark 3-5
Eucalyptus torquata	Flowering gum	Australia	Leaves 10 Bark 17
Eucalyptus viminalis	Manna gum	New South Wales	{ Bark 4-8 Kino 69 Leaves 4
Eugenia braziliensis	Yhva-poroitih	Paraguay	Bark 43 Leaves 17 Wood 12
Eugenia jambolana Eugenia jambos Eugenia maire	Java plum	India Brazil New Zealand	Bark 19 Bark 12 Bark 16-17 Bark 29
Eugenia michellii Eugenia pungens Eugenia smithii	Nangapirih gwazu Yhva viyu	Paraguay Paraguay	Bark 11
Eugenia sp.	Yhvajhay puihta gwazu		Bark 17 Bark 16-29
Exocarpus cupressiformis Fiscus sp.	Native cherry Kili bark	Australia Sudan	Bark 15-23 Bark 19
Fusanus acuminatus Garicinia mangostana	Quandony Mangoustan	Australia Cochin China	Bark 19 Fruit shells 14
Grevillia striata Guarca sp.	Beefwood Guare	Australia Paraguay	Bark 18
Hakea glahella Hakea leucoptera	Prickly pear Needle bark	Australia New South Wales	Bark 18-20
Heritiera fomes	Sundri bark	India	Bark 10 Bark 18-20 Bark 11 Bark 7
Hopea odorata		India	Leaves 11
Hopca parviflora Hydnora longicollis	Ironwood	India	Wood 10 Bark 17-22
Inga affinis	Ganib Inga gwazu	Africa Paraguay	Roots 32 Bark 26

Table 23—(Continued)

Table 23—(Continued)						
Botanical Name	Place Grown	Per cent Tannin				
Inga feuillei Juniperus recurva Krameria triandria Larix dahurica Larix europaea	Paypay Weeping blue Rhatany Larch Larch	Peru Japan Peru Japan Europe	Pods 12-15 Bark 8 Root bark 20 Bark 9 Bark 9-10			
Larix occidentalis	Western larch	N. W. United States	Bark 11 Wood 7			
Laurus lingue Leuceadendron argenteum Leucospermum conocarpum Ludwigia caparossa Lysiloma candida Maclura pomifera Malpighia faginea Malpighia punicifolia Mimosa farinosa Mimosa pudica Mimosa sp.	Silver tree Knotted tree Caparossa Palo blanco Osage orange Nance Mangrutta Mimosa Mimosa Yukeri gwazu	Chile Cape Good Hope Cape Good Hope Brazil Lower California Texas Mexico Nicaragua Argentina India Paraguay	Bark 17-19 Bark 9-16 Bark 10-22 Bark 20-25 Bark 26 Wood 11 Bark 26 Bark 20-30 Bark 4 Roots 10 Bark 11			
Myrica asplenifolia	Sweet fern	Michigan	{Leaves 4-5 Roots 4-6			
Myrica nagi Nauclea gumbir Ocotea bullata Ocotea sp Osyris abyssinica	Box myrtle Gambier Yhva-iha	India East Indies South Africa Paraguay Transvaal	Bark 13-27 Leaves and twigs 5-6 Bark 6 Bark 11 Leaves and twigs 13-25			
Osyris arborea Osyris compressa Oxalis gigantea Paullinia sorbilis Peltophorium dubium	Cape sumac Guara Yhyihra puihta	Northern India Cape Good Hope Chile Brazil Paraguay	Leaves 20 Leaves 17-23 Bark 25 Fruit 43-55 Bark 31			
Pentacme suavis		India	Leaves 12-24 Bark 7-13 Wood 4 Stoned fruit 26-35			
Phyllanthus emblica	Amla	India	Stoned fruit 26-35 Leaves 23-28 Bark 15-24			
Phyllocladus asplenifolia Phyllocladus rhomboidalis Phyllocladus trichomanoides Picea glehni Picea sitchensis Pinus cembra Pinus densiflora Pinus halepensis Pinus Khasya Pinus Khasya Pinus Ingifolia Pinus muricata Pinus radiata Pinus radiata Pinus riuma pinus riuma Pinus sylvestris Pinus thunbergii Piptadenia cebil Piptadenia rigida Pistacia lentiscus Pitacia orientalis Pithecolobium dulce Polygonum amphibium	Celery-topped pine Celery-topped pine Red yezomatsu Sitka spruce Pine Red pine Aleppo pine Pine Long-leaved pine Swamp pine Monterey pine Scotch fir Black pine Kurupaih-ra puihta Pistacio Pistacio Camanchile	Tasmania Tasmania Tasmania New Zealand Japan Pacific states Alpine Europe Japan Mediterranean coasts Burma India California California Northern Europe Japan Argentina Paraguay Mediterranean India Mexico Missouri	Bark 23 Bark 15-21 Bark 28-30 Bark 19 Bark 12-18 Bark 3-5 Bark 6 Bark 10-20 Bark 11-14 Bark 13 Bark 14 Bark 4-5 Bark 6 Bark 15 Bark 28 Leaves 12-19 Galls 30-40 Bark 15-25 {Roots 22			
Polygonum ampnioium Polygonum bistorta	Snakeweed	Missouri England	Branches 17 Roots 16-21			
Polythus tremula Prosopis oblonga Protea grandiflora Protea mellifera Pseudotsuga taxifolia	Snakeweed Poplar Abu-surug Sugarbush Douglas fir	Europe Sudan Cape Good Hope Cape Good Hope Pacific states	Bark 3 Bark 14 Bark 15-16 Bark 18-25 Bark 7			
Punica granatum	Pomegranate	India	Fruit rind 27-30 Kernel 32 Bark 18-22			
Quebrachia lorentzii Quercus aegilops Quercus agrifolia Quercus alba Quercus californica Quercus cerris Quercus chrysolepis Quercus coccifera Quercus coccinea Quercus densiflora Quercus dentiflora Quercus dentiala	Quebracho Valonia Live oak White oak Black oak Turkey oak Maul oak Kermes oak Scarlet oak Tanbark oak	Argentina and Paraguay Mediterranean California Northern America California Southern Europe Pacific states Mediterranean United States California Japan	Wood 20-30 Bark 6-8 Acorns 17-40 Bark 19 Bark 7 Bark 7 Bark 10 Galls 35 Bark 7-12 Bark 10-18 Bark 8 Bark 8 Bark 10-29 Bark 11 Wood 7			
Zwerens aemouna	Japanese oak	Japan	l Wood 7			

Table 23 (Continued)

Botanical Name Common Name Place Grown Per cent Tannin	Table 23—(Continued)						
Quercus prinus Quercus prinus Quercus prinus Quercus flora Quercus indicata Q	Botanical Name	Place Grown	Per cent Tannin				
Overcus incoma Quercus infectoria Quercus mirbecki Quercus mirbecki Quercus mirbecki Quercus prinus Quercus subra Quercus pp. Quercus subra Quercus pp. Quercus subra	Quercus garryano		Pacific states	Bark 6-7 f Bark 9			
Quercus prinus Quercus prinus Gequang Gept Gercus obser	Quercus incana Quercus infectoria Quercus lamellosa Quercus lineata Quercus lobata	Aleppo Hill oak	India Turkey Northern India Northern India California	Bark 5-11 Bark 22 Galls 24-60 Bark 8-10 Bark 11 Bark 12			
Quercus prims Chestnut oak United States Bark 9-12 Quercus robur Common oak Europe and U. S. Bark 10 Quercus rubra Red oak Northern America Twig galls 35 Quercus suber Gie-bob Indo-China Bark 4-6 Quercus suber Cork oak Europe Bark 12-19 Quercus velutina Highland oak United States Bark 12-19 Quercus velutina Highland oak United States Bark 6-12 Quercus velutina Highland oak Paraguay Bark 6-12 Rhizophora manyle Mangrove (Cutch) Tropical coasts Bark 22-3 Rhizophora mucronata Mangrove (Cutch) Australia, Asia and Africa Bark 22-32 Rhus coriaria Sieilian sumae Vinited States Leaves 25-32 Rhus cotinus Venetian sumae United States Leaves 17-38 Rhus apentaphylla Tixra sumae Morocco White sume United States Leaves 17 Rhus seenialata Sumae Sumae New South Wales Rust 23 <t< td=""><td></td><td>Sungra katus</td><td></td><td>Acorn cups 13-15 { Bark 12-13</td></t<>		Sungra katus		Acorn cups 13-15 { Bark 12-13			
Quercus rubra Red oak Northern America Ruig galls 35 (Bark 12 - 10 oct of the control of the cont	Quercus prinus Quercus pseudocornea			Bark 9-12 Bark 16			
Quercus suber Quercus suber Quercus suber Quercus velutina Quercus Quercu	Quercus robur	Common oak	Europe and U. S.	Wood 2-4			
Quercus suber Quercus velutina Quercus velutina Quercus velutina Quercus velutina Quercus velutina Rheedala brasiliensis Rhizophora manule Rhizophora Rhizophora manule Rhizophora Rhizophora manule Rhizophora Rhizophor			Northern America	Twig galls 35 Bark 4-6			
Rhisophora matry Mangrove (Cutch) Rhisophora matronata Mangrove (Cutch) Rhus copallina Rhus copallina Sumac Rhus coriaria Sieilian sumac Rhus cotinoides Sumac Rhus cotinoides Sumac Rhus cotinus Venetian sumac Rhus cotinus Runac Rhus cotinus Rhus cotinus Runac Rhus semialata Runac Rhus semialata Runac Rhus semialata Runac Runac Rhus semialata Runac Rhus semialata Runac Runac Rhus semialata Runac Runac Rhus semialata Runac Run	Quercus suber Quercus tozac Quercus velutina Quercus wislizeni Rheedia braziliensis	Cork oak Black oak Highland oak Pakuri	Europe Southern France United States California Paraguay	Bark 12-19 Bark 14 Bark 6-12 Bark 7-8 Bark 22 Bark 26-32			
Rhus copallina Rhus coriaria Rhus coriaria Rhus cotinoides Sumac Rhus cotinoides Sumac Rhus cotinoides Sumac Rhus cotinoides Sumac Rhus cotinoides Rhus mysorensis Rhus pontaphylla Tizra sumac Rhus semialata Rhus semialata Rhus semialata Rhus thunbergii Robinia pseudacacia Rlack Locust Rollinia sp. Aratiku gwazu Rumar hymenoscpahum Rumar maritima Docks Sabal palmetto Sabal servulata Salix arenaria Willow Salix arenaria Salix ragiis Salix reproac Willow Salix reproac Sal	Rhisophora manyle	Mangrove ((*utch)	Tropical coasts				
Rhus cotinoides Rhus glabra Rhus glabra Rhus mysorensis Rhus pentaphyula Rhus pentaphyula Rhus semialata Rhus semialata Rhus semialata Rhus semialata Rhus semialata Rhus thunbergii Rhus thunbergii Rhus thunbergii Robinia pseudacacia Rollinia sp. Rumac Rumac kymenosepahun Russia Rumac kymenosepahun Russia Rumac kymenosepahun Russia Rark 13 Salix arenaria Salix fragitis Willow Salix fragitis Willow Russia Bark 8-12 Rark 9-12 Salix purpurea Salix purpurea Salix purpurea Willow Salix purpurea Willow Russia Bark 8-12 Rark 9-12 Rark 9-12 Rark 9-12 Rark 9-12 Rark 1-3 Rark 1-3 Rark 9-12 Rark 1-3 R	Rhus copallina	Sumac	Africa United States	Bark 21-48 Leaves 17-38			
Rhus semialata Rhus semialata Sumac Sumac India Cape Good Hope Rhus thubergii Rhus thubergii Rhus thubergii Rhus thubergii Rhus secadanea Rhus thubergii Rhus thubergii Rhus thubergii Robinia pseudacacia Black Locust Black Locust Europe Bark 28 Leaves 20 Bark 27 Wood 3-4 Rottina sp. Rottina sp. Rottina sp. Rumer hymenoscophum Rumer maritima Docks Cabbage palmetto Sabal palmetto Sabal palmetto Sabal palmetto Salir arenaria White willow Salir arenaria Willow Salir arenaria Willow Salir fragilis Salir fragilis Salir pripurea Salir pripurea Salir pripurea Salir pripurea Willow Salir pripurea Salir pripurea Willow Salir pripurea Salir pr	Rhus cotinoides Rhus cotinus Rhus glabra Rhus metopium Rhus mysorensis	Sumac Venetian sumac White sumac Sumac	United States Italy United States United States United States	Leaves 21 Leaves 17 Leaves 15-25 Leaves 8			
Rhus semialata Rhus succedanea Rhus thurbergii Rhus typhina Rhus peudacacia Rhus peudacacia Rlias peudacacia Rumer maritima Rumer maritima Sabal palmetto Sabal palmetto Salir arcaria Salir arcaria Salir fragilis Salir caproca Salir purpurea Salir minalis Salir minalis Salir minalis Schimus molle Sequoia sempervirens Redwood Rods gum Redwood Rods gum Rumer purpurea Salir lindia Salir purpurea Salir purpurea Salir purpurea Salir purpurea Salir purpurea Salir minalis Salir minalis Solica corpocia Salir sumpalis Salir sumpalis Salir purpurea Sa				Wood 23			
Rhus succedanea Rhus thunbergii Rhus thunbergii Rhus typhina Robinia pseudacacia Rollinia sp. Rollinia sp. Rumex hymenoscpalum Rumex maritima Sabal palmetto Sabal palmetto Salix aceptoca Salix aceptoca Salix ragilis Salix alix alix alix alix alix alix alix				Bark 23 f Leaves 5			
Robinia pseudacacia Black Locust Europe Wood 3-4 Rollinia sp. Aratiku gwazu Paraguay Bark 4 Rumex hymenoscpalum Rumex maritima Docks Europe Roots 22 Sahal palmetto Cabbage palmetto Florida Roots 10-18 Sabal parrulata Saw palmetto Florida Leaves 13 Salix arenaria Willow Russia Bark 9 Salix arenaria Willow Japan Bark 8-12 Salix fragilis Willow Japan Bark 8-12 Salix fragilis Willow Japan Bark 8 Salix purpurea Yellow willow Russia Bark 9 Salix invinalis Willow Japan Bark 8 Salix viminalis Willow Russia Bark 7-10 Schinus molle Argentina Leaves 19 Sequoia sempervirens Redwood Pacific states Sapwood 1-2 Bark 1-3 Shorea obtusa Sal bark India Bark 6-15 Shorea robusta Sal bark India Bark 6-15 Spermolepsis gummifera Oak gum New Caledonia Sark 17 Statice coriaria Marsh rosemary Southern Russia Bark 17 Statice coriaria Marsh rosemary Southern Russia Bark 18-27 Tamarix africana Tamarisk Mediterranean Galls 43-56 Tamarix africana Tamarisk Morocco Galls 43-56 Tamarix africana Tamarisk Morocco Galls 43-56 Tamarix cuspidata Yew Japan Bark 10 Tarus cuspidata Yew	Rhus succedanea Rhus thunbergii	Sumac	India Cape Good Hope	Leaves 20 Bark 28			
Rollma sp. Rumex hymenoscpalum Rumex hymenoscpalum Rumex maritima Docks Sabal palmetto Salix alba Salix aronaria Willow Salix aronaria Willow Salix fragilis Salix fragilis Salix parpurea Salix purpurea Salix purpurea Willow Salix viminalis Salix viminalis Sequoia sempervirens Redwood Redwood Pacific states Sapwood 1-2 Sapwood 1-	Robinia pscudacacia						
Salix viminalis Schinus molle Molle Russia Argentina Redwood Russia Argentina Redwood 4-12 Sapwood 1-2 Bark 7-10 Redwood 4-12 Sapwood 1-2 Bark 1-3 Shorea obtusa Shorea robusta Sonneratia payatpat Spermolepsis gummifera Statice coriaria Statice coriaria Stryphnodendron Barbatimao Marsh rosemary Barbatimao Tamarix africana Tamarisk Morocco Tamarix africata Tamarisk Tamarix dioica Taxus cuspidata The dwood Argentina Redwood Russia Rodd 6-7 Rark 1-1 Rodd 6-7 Rark 6-15 Rark 1-1-12 Rark 11-12 Spermolepsis gummifera Oak gum New Caledonia Rark 11-12 Southern Russia Roots 20-22 Bark 18-27 Galls 26-56 Twigs 9 Leaves 9 Leaves 9 Calls 43-56 Rark 10 Rark 10 Rark 10 Rark 10	Rumex hymenosepalum Rumex maritima Sabal palmetto Sabal serrulata Salix alba Salix arenaria Salix caproca Salix fragilis Salix lasiandra	Canaigre Docks Cabbage palmetto Saw palmetto White willow Willow Willow Willow Yellow willow	Mexico Europe Florida Florida Russia Japan California	Bark 4 Roots 25-30 Roots 22 Roots 10-18 Leaves 13 Bark 9 Bark 13 Bark 8-12 Bark 9-12 Bark 2			
Sequoia sempervirens Redwood Pacific states Sapwood 1-2 Sapwood 1-2 Sapwood 1-2 Sarwood 1-2 Sarw 1-3 Sarw 1-3 Someratia pagatpat Sark 9 Wood 6-7 Someratia pagatpat Philippines Bark 6-15 Sarw 1-12 Spermolepsis gummifera Oak gum New Caledonia Statice coriaria Marsh rosemary Southern Russia Roots 20-22 Stryphnodendron Barbatimao Brazil Roots 20-22 Bark 18-27 Tamarix africana Tamarisk Mediterranean Tamarisk Mediterranean Tamarix africata Tamarisk Morocco Galls 26-56 Tamarix aticulata Tamarisk Morocco Galls 43-56 Tamarix cuspidata Tawas cuspidata Yew Japan Bark 10	Salix viminalis	Willow	Russia	Bark 7-10			
Shorea obtusa Shorea robusta Shorea robusta Someratia pagatpat Sal bark Someratia pagatpat Spermolepsis gummifera Statice coriaria Statice coriaria Statice coriaria Statice coriaria Marsh rosemary Southern Russia Bark 17 Kino 43-80 Roots 20-22 Stryphnodendron Barbatimao Barbatimao Tamarix africana Tamarisk Mediterranean Tamarisk Morocco Tamarix articulata Tamarisk Morocco Calls 43-56 Tamarix dioica Tavus cuspidata Tew Tamarix uni dioica Tavus cuspidata Temarix uni dioica Tavus cuspidata Tamarix uni dioica Tavus cuspidata Tamarix dioica Tavus cuspidata Tavus cuspidata Tavus dioica Tavus cuspidata Tavus dioica Tavus cuspidata				[Heartwood 4-12			
Sonera robilità Soneratia pagatpat Solitaria S	Shorea obtusa		India	Bark 9			
Statice coriaria Marsh rosemary Southern Russia Roots 20-22 Stryphnodendron Barbatimao Brazil Bark 18-27 Tamarix africana Tamarisk Mediterranean Tamarisk Morocco Galls 43-56 Tamarix atoica Ihao India Bark 10 Tawas cuspidata Yew Japan Bark 10		Sal bark Pagatpat		Bark 6-15			
Statice cordaria Stryphnodendron barbatimao Tamarix africana Tamarisk Tamarix articulata Tamarisk Morocco India Tavus cuspidata Tavus cuspidata Tavus cuspidata Marsh rosemary Brazil Southern Russin Roots 20-22 Bark 18-27 Bark 18-27 Roots 20-22 Bark 18-27 Bark 18-27 Morocco Galls 43-56 India Bark 10 Bark 10	Spermolepsis gummifera	Oak gum	New Caledonia	Bark 17			
Tamarix articulata Tamarisk Mediterranean Twigs 9 Tamarix articulata Tamarisk Morocco Calls 43-56 Tamarix dioica India Bark 10 Taxus cuspidata Yew Japan Bark 10	Stryphnodendron		Southern Russia Brazil	Roots 20-22 Bark 18-27			
Tamarix arriculata 1 amarisk Morocco Galls 43-56 Tamarix dioica Jhao India Bark 10 Taxus cuspidata Yew Japan Bark 10	Tamarix africana	Tamarisk	Mediterranean	{ Twigs 9			
	Tamarix dioica Taxus cuspidata	Jhao Yew	India Japan	Galls 43-56 Bark 10 Bark 10			

Table 23—(Continued)

Botanical Name	Common Name	Place Grown	Per cent Tannin
Terminalia belerica Terminalia catappa Terminalia chebula Terminalia glabra Terminalia mauritiana	Bedda Badamier Myrobalans Kumbuk Jamrosa	India India India Ceylon India	Nuts 12 Bark 12-25 Nuts 30-40 Bark 27-32 Bark 30
Terminalia oliveri	Thann	Malay	{ Bark 31 Leaves 14
Tornentilla erecta Trichilia catigua Trichilia hieronymi Tsuga canadensis Tsuga heterophylla Umbellularia californica Vateria indica Weimannia glabra	Kaatigua puihta Kaatigua moroti Hemlock Western hemlock California laurel Curtidor	Europe Paraguay Paraguay Northern America Pacific states California India Venezuela	Roots 20-46 Bark 21 Bark 23 Bark 7-12 Bark 9-16 Bark 16 Fruit 25 Bark 10-13
Woodfordia floribunda	Itcha	India	{ Bark 27 Leaves 15
Ximenia americana	Alimu	Sudan	Bark 17
Xylia dolabriformis	Jamba	Burma and India	$\begin{cases} \text{Bark 9-19} \\ \text{Wood 4} \end{cases}$
Xylocarpus granatum Xylocarpus obovatus Zizyphus nummularia Zizyphus xylopyra	Piagao Tabique Ber Gothar	Africa and Asia Philippines India India	Bark 21-48 Bark 22-25 Bark 10 Fruit flesh 23

in abundance. In the majority of cases, at least, the tannin contents are supposedly those of the air-dried material.

The tannin contents given in Table 23 were determined by methods similar in principle to that of the American Leather Chemists' Association, on which most tanning materials are bought and sold in the United States and which will be discussed below. As it may be assumed that nearly every form of plant life contains some tannin, the list cannot be considered complete; but it contains most of the materials cited in the literature which contain enough tannin to make them interesting as possible sources for tannin on a commercial basis.

Of the vegetable tanning materials listed above from 336 different species of plant life, probably less than 20 are used in the United States on a large scale.

Table 24. United States Production, Imports and Values of Tanning Materials and Extracts for 1937.

	T		ъ	T
	pounds	dollars	pounds	Production-
			•	dollars
Quebracho wood, extract	142,412,184	\$4,627,715	81,226,404*	\$1,404,418
Quebracho wood, raw	27,310,000	208,602		
Chestnut wood extract			363,706,338	4,968,487
Mangrove bark, extract	15,517,948	431,405		
Mangrove bark, raw	10,288,652	92,775		
Myrobalans, extract	1,284,261	46,736	3,473,508*	81,278
Myrobalans, raw	41,174,000	395,960	.,,	01,2.0
Wattle bark, extract	5,429,487	182,747	3,690,238	76,339
Wattle bark, raw	18,709,943	229,143	-,,	. 0,007
Valonia, extract	701,882	35,629		
Valonia, raw	25,429,193	379,823		
Oak bark, extract	,,	0,7,020	12,698,305	346,286
Oak bark, raw	990	12	,-,-,	0.0,200
Hemlock bark, extract			7,706,032	194,596
Hemlock bark, raw	1,564,580	5,157	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	171,070
Gambier, extract	2,00.,000	5,257	777,722	53,611
Gambier, raw	4.615.866	319.097	777,720	50,011
Sumac, raw	3,192,000	81,056	3,538,350	169,330
Divi-divi, raw	96,620	1,534	5,556,556	107,550
Other materials, extract	114,080	4,676	12,828,000†	505,734
Other materials, raw	42,375	1,223	12,020,0001	303,734
Omer materials, law	72,373	1,225		
Totals	297,884,161	\$7,043,290	489,644,259	\$7,800,079

^{*} Data for 1935; productions of quebracho and myrobalans extracts were not listed by the Bureau of the Census in 1937, in order to avoid disclosures of the activities of individual establishments. † Estimate only; quantity is not given by the Bureau of the Census. In the domestic production of the extracts of quebracho, myrobalans, wattle, gambier and sumac, the raw materials were imported.

American Survey

Mr. E. G. Holt, Chief of the Leather and Rubber Division of the Bureau of Foreign and Domestic Commerce, has furnished the writer with the data on United States production and imports of tanning materials and extracts for 1937 shown in Table 24.

The quantity values for the extracts have only a limited significance because they do not differentiate between the solid and liquid extracts and the domestic extracts made from foreign raw materials are apparently also included in the imports of raw materials.

In order to provide more significant information on the approximate annual consumption of tannin from different sources by the tanners of the United States, the writer secured the data given in Table 25 from Mr. Alan Goldsmith, President of the American Tanning Extract Manufacturers' Association. For direct comparison, the values are calculated to tons of material of 25 percent tannin content. For some materials, the quantity used by the tanner in the form of raw material is also given. The total includes both extract and raw material.

Table 25. Consumption on Tannin Basis of Tanning Materials by United States Tanners in the Calendar Year of 1939.

As tons of	of 25% tannin
total	raw material
176,500	
123,000	
21,750	5,750
18,500	3,500
15,250	10,500
14,500	12,500
12,000	,
7,000	
4,000	
4,000	
3,000	
	total 176,500 123,000 21,750 18,500 15,250 14,500 12,000 7,000 4,000 4,000 4,000

^{*} Most of the sumae was imported and used as ground, raw leaves, but no data are available as to the amount converted and used as extract. Other materials were used in too small amounts to be included in this survey. Of the quebracho extract, from 25,000 to 50,000 tons were produced in the United States from imported logs. No data are available for raw hemlock and oak barks used by the tanners.

Quebracho

Although first used as a tanning agent only 70 years ago, the extract from the quebracho tree (Quebrachia lorentzii) furnishes more tannin to the leather world than that from any other form of plant life. The wood of the quebracho tree is very rich in tannin of high purity, the heart wood containing from 20 to 24 percent tannin by weight. The name quebracho comes from the Portuguese and means "break ax," the wood being so hard that it will turn the edge of a good ax. It is also the heaviest wood known, a cubic foot of it weighing from 79 to 84 lbs. A cubic foot of water weighs only 62.3 lbs. and so quebracho wood will not float in it. All our quebracho comes from South America. According to Durland, the quebracho forests of northern Argentina and southern Paraguay have the distinction of being the only forests of their kind in existence. Thus practically all the world's supply of this valuable wood comes from this region.

Quebracho trees seldom form a dense stand, but are usually found scattered through open mixed forests of hard woods. The peculiar V-shaped crowns of quebracho tower many feet above the other hard-wood trees and form a distinctive feature of the landscape. It is unusual to find more than 4 or 5 of these trees to an

acre of ground. They average from 35 to 40 feet in height, but many trees range from 50 to 75 feet in height and from 2 to 4 feet in diameter.

Being the hardest, heaviest and most durable wood known, quebracho is used for many purposes other than as a source of tannin. Durland estimated the annual consumption of quebracho wood for all purposes at about one million tons, and that about 150 years would be required to exhaust the supply at that rate. However, the possibilities of reforestation are good.

Most of the quebracho extract for tanning is produced right in the Argentine, but some wood is imported into the United States for extraction here. In making the extract, the red heartwood is first chipped and then ground to a fine state of division. The ground material is placed in batteries of rotary diffusors and extracted with water and steam under pressure until practically all the tannin has been extracted. The spent material is used as fuel.

The tannin liquor is run first into settling tanks and then pumped into evaporators of double, triple or quadruple effects where it is concentrated to a strength of about 25° Baumé. It is then of a syrupy consistency and is run into the finishing evaporators, where it is heated and stirred for about 10 to 14 hours under a vacuum until the water content is reduced to such point that it will solidify upon cooling. The vacuum is broken and the extract is allowed to flow into bags held on scales below. As each bag is filled, it is sewn up and placed on a rack to cool and solidify. In this form, it is shipped to the tanners.

The large amount of heat used in producing the solid quebracho extract causes the conversion of some of the soluble constituents into insoluble material. Many tanners render this material soluble again by a process of bisulfiting, which will be described later. One plant in the United States imports quebracho wood to produce a liquid extract in which precipitation of nontannins has been avoided by the application of less heat; some tanners find this liquid extract better suited for their use than the solid extract. It is readily diluted with water for use and does not require bisulfiting.

Chestnut Wood

The most important domestic source of tannin in the United States is the wood of the American chestnut tree, Castanca dentata. In the tanneries of the United States, the consumption of chestnut is second only to that of quebracho. The chestnut tree is found in abundance in Virginia, North Carolina, Tennessee and in the northern parts of Georgia and Alabama. Unfortunately, this tree is threatened with extinction by a fungus importation from the orient, called Chestnut Blight. This blight has been spreading for the past 30 to 40 years and there is no hope in sight that it will be checked. Because the dead wood can be used for making tanning extracts, it is estimated that it will remain an important source of tannin for the next 15 to 20 years, and possibly longer. The chestnut tree is able to reproduce itself, by sprouting from the stump, within a period of 20 years. If the blight could be checked, it would form an almost inexhaustible supply of tannin. Analyses of the tannin contents of wood from different parts of the tree were made by Frey and Leinbach and are included in Table 23.

The manufacture of extract from the wood is similar in principle to that used in making quebracho extract. Most chestnut extract is sold to the tanners in liquid form containing about 25 percent tannin, but some plants are equipped to reduce it to the solid state of about 65 percent tannin. The present capacity in the United States for reducing liquid extract to the dry state is estimated at about 50,000 tons of liquid extract annually.

Mangrove Bark

Mangrove bark extract for tanning purposes is obtained from the bark of several species of *Rhizophora*, or mangrove tree. Although mangrove trees are found in many tropical countries, they vary greatly in value as a source of tannin. Probably the most important source at the present time is Borneo, the second largest island in the Malay Archipelago. Here modern extract-manufacturing plants extract the tannin from the bark and ship it to the United States and other countries under the name of *Cutch Extract*. It is a solid extract containing 55 percent of tannin. Less than 40 years ago, mangrove bark and cutch extract were among the less common of the vegetable tanning materials, but today they stand third in order of quantity consumed in the United States. In Germany in 1904, Dr. Johannes Paessler demonstrated the superior tanning qualities of mangrove cutch over oak bark, and this started an active interest in the studies which have since led to the discoveries of the remarkable tanning properties of cutch extract, which make it unique among all vegetable tanning materials. These properties will be discussed later in this chapter.

Myrobalans

The dried nuts of the Terminalia chebula of India, called myrobalans, are rich in tannin and in highly fermentable sugars. Many sole-leather tanners use myrobalans in quantity, not so much for its tanning properties as for the organic acids which it produces in the tan liquors by fermenting. In Chapter 9, it was pointed out that many sole-leather tanners do not delime their stock before putting it into the vegetable tan liquors and so require a source of acid to take care of the lime in the tan yards. Some tanners make up special storage tanks of myrobalans liquors and allow them to ferment, forming organic acids. With these liquors, they control the pH values of the tan liquors. They mix the myrobalans liquor with their stock tan liquor and increase the proportion when they desire to lower the pH value of the tan liquors in use and decrease the proportion when they desire to raise the pH value. About 90 percent of the myrobalans imported into the United States is received as raw material, and most of this is converted into extract before it reaches the tanner. Of the amount consumed by the tanners, about 19 percent is received by the tanners as raw material, and the tanners leach it themselves to make the acid-forming liquors.

Wattle Bark

Various species of Acacia known as wattle trees have barks that are very rich in tannin of high purity. Although found originally in Australia, transplantations into South Africa have been so successful that Natal has now become an important source for this valuable tanning material. Wattle is imported into the United States both as solid extract and as raw bark. Extract manufacturers in the United States convert some of the imported bark into extract. American tanners receive about 70 percent of the total wattle they use as raw bark and leach it themselves; the remaining 30 percent is received as concentrated extract.

Valonia

Sixth in volume consumption in the United States is Valonia, which is obtained from the cups and beards of the acorns of the Turkish oak, Quercus aegilops, which grows in the region of Asia Minor. Most of the valonia imported into the United States arrives as raw cups and beards, although a relatively small amount is received as extract. Domestic manufacturers convert about 15 percent of the raw material into extract and the rest is received by the tanners as raw material, with

the cups separated from the beards. It is an acid-forming material and is used not so much for its tanning value as for its filling properties, its acid and for the pleasing color it adds to the leather.

Spruce Extract

Although spruce bark contains from 7 to 15 percent of tannin, the wood untreated appears to contain very little. Spruce wood is used on an enormous scale to make paper. The cellulose fibers of the wood are leached with solutions of lime and sulfur dioxide in order to remove the lignins, which would have a deleterious effect upon the paper, if not removed. The action of the lime and sulfur dioxide upon the lignins renders them water-soluble, in which form they are known as lignosulfonic acids. The liquors obtained from the extraction of the spruce fibers are known as waste sulfite liquors and have presented serious problems of disposal to paper manufacturers.

However, it was discovered that these liquors when properly prepared have excellent tanning properties. Hurt prepared waste sulfite liquors for tanning as follows: The liquors contain calcium lignosulfonates and free acid. The free acid was neutralized by adding lime, and the liquor was then evaporated, under vacuum, to a gravity of 32° Baumé. The calcium content was then determined and somewhat less than its equivalent of strong sulfuric acid was added while stirring, most of the lime being precipitated as calcium sulfate. The lime then remaining in solution was precipitated by adding the calculated amount of sodium bisulfate. The liquor was then stirred for several hours longer and filter-pressed to remove the precipitated matter, consisting chiefly of calcium sulfate. The liquor thus purified is sold as a tanning agent under the name of spruce extract.

This extract was developed by Robeson Process Co., who then developed both a liquid and solid extract under the name of *super-spruce extract*, representing a higher degree of refinement than the spruce extract. This was followed, in turn, by the development of a liquid extract known as *LacTan-X*, in whose process of manufacture bacterial cultures are used to convert the sugars into lactic and acetic acids. A typical sample contains 25 percent tannin, $4\frac{1}{2}$ percent lactic acid and $2\frac{1}{2}$ percent acetic acid.

Another product made from the waste sulfite liquors is known as *goulac*. The liquors are neutralized and reduced to dry powder containing only about 3 percent of water.

Most vegetable-tanning extracts are blended with others in actual use. When so blended, the spruce extracts compare favorably in tanning properties and in the quality of the leather they produce. In 1939, they ranked seventh in order of quantity consumed in the United States.

Oak Bark

Oak bark, once a major source of tannin in the United States, has now fallen into eighth place. It was obtained from the common oak, Quercus robur, the tanbark oak, Quercus densifiora, and the chestnut oak, Quercus prinus. Part of the falling off in its use may be attributed to its increasing scarcity, and part to the fact that some of the newer extracts produce results that are more satisfactory as well as more economical. Because of a demand for spent oak bark by other industries, some tanners still use raw oak bark, extract the tannins themselves and then find that they can sell the spent bark for as much as they paid for it originally. California tanners apparently still use local bark as their chief tanning material.

Practically all the oak bark used in this country is of domestic production.

Hemlock Bark

The bark of the hemlock tree, *Tsuga canadensis*, once furnished many American tanneries with their only source of tannin. It was customary to locate tanneries close enough to hemlock forests and lumbering districts so that the bark could be obtained with a minimum hauling charge. Many such tanneries today use no hemlock bark at all. Like oak bark, hemlock bark has become increasingly scarce and some bark is being imported, apparently from Canada, to help out the domestic supply. Hemlock bark has fallen into ninth place in volume consumption in the United States.

Gambier

One of the mildest tanning materials known is gambier extract, which is obtained from the leaves and twigs of the *Nauclea gambir*, found in the East Indies. The trees grow to a height of about 10 feet. The twigs and leaves are treated with boiling water and the extract is strained and then thickened with rice meal. For some grades, the paste is baled and for others it is cut into cubes and dried, when it is known as *cube gambier*. The finest grade is known as *Plantation gambier*.

It is a relatively expensive material and produces very low yields of leather when used alone, but it penetrates very heavy hides rapidly and is capable of producing leathers of enormous strength.

Sumac

The sumac of commerce consists of the dried and ground leaves of *Rhus coriaria* cultivated on the island of Sicily. Although some of it is converted into extract, many tanners use only the raw material, steeping it in warm water just before using it, as in making tea. Sometimes they use the liquor after straining from the insoluble residue and sometimes use residue and all. Like gambier, it is an extremely mild tanning material. It is sometimes used as the only tanning material for skivers and very thin skins used for bookbinding, hat bands, etc. For heavier leathers, it is used chiefly as a mordant in dyeing.

Divi-divi

The pods of the divi-divi tree, Caesalpinea coriaria, of Central America and Brazil, serve a purpose similar to that of myrobalans. They are rich in tannin and form acids very readily by fermentation. They are received by the tanner in the raw state and used chiefly to produce acids. However, their use during the past 20 years has decreased markedly, while that of myrobalans has increased.

Leaching Raw Tanning Materials

Years ago it was customary to locate tanneries near large supplies of raw tanning materials, particularly forests from which trees were being cut for lumber and an abundant supply of bark was available as waste. The modern tanner, however, requires a variety of tanning materials in highly purified and concentrated forms. There are now many highly efficient tanning-extract plants all over the world with modern equipment and procedures capable of providing the tanner with extracts better suited to his purpose and at lower cost than he can produce them himself. Today American tanners purchase more than 90 percent of their tanning materials in the form of concentrated extracts. However, many tanners still find it advantageous to leach some raw materials to produce liquors which they strengthen for use with concentrated extracts.

One of the oldest systems for leaching raw materials, and the one most commonly used in tanneries, is known as the open vat method. The bark, or other

material, is broken into small pieces and then shredded in a bark mill. The leaching tanks are usually arranged in batteries of about eight and are fitted with perforated false bottoms on which the bark is placed. The bottom of each tank is fitted with a pipe through which liquor may be drawn off or pumped from one tank to another. When fresh bark is put into a given tank, liquor is run onto it which has been used to leach the bark in all of the seven other tanks. This strong liquor is finally drawn off and pumped into a storage tank. The bark is then leached with liquor which has passed through only six other tanks. The eighth leaching of this bark is made with fresh water, after which the bark is dumped and discarded.

Fresh water is used to leach only the most nearly exhausted bark. As the liquor becomes stronger in tannin, it is run onto fresher bark, and finally onto the previously unleached bark. As soon as each tank is dumped, it is again filled with fresh bark and becomes the head vat in the cycle, which is continuous. The object of this system of leaching is to get final liquors as concentrated as possible. In the tannery, the liquor in the storage tank is used as needed, but in the extract plant it is necessary to evaporate off most of the water so as to make its subsequent transportation practical.

The extraction of the raw material is often facilitated by the use of mechanical devices. Sometimes the leaching tanks are equipped with mechanical stirrers or with pipes for bubbling air up through the liquor. In another system, the tanks are replaced by revolving drums, used on the same principle as the open vats, the liquor being pumped from one drum to another. In still another system, the bark, or other material, is forced through a trough in one direction, by means of a screw conveyor, while water flows over the bark in the opposite direction. At the point of entry of the fresh water, the bark is practically exhausted and is dumped onto a pile from which it is subsequently moved to the furnaces for fuel, or is disposed of in some other way. At the point of entry of the bark, the liquor is richest in tannin and is conducted to the storage tank.

The rate at which tannin can be extracted from the raw material increases with the temperature of the water used, but so also does the rate at which the dissolved matter decomposes. The variation of the ratio of these two rates with temperature determines the optimum temperature that it is desirable to employ and this is different for different materials. It is customary to extract the fresh material at a low temperature and to increase the temperature of extraction until the material is practically exhausted. In using the open vat system for ordinary barks, it is a good plan to have the fresh water at the boiling point and to allow its temperature to fall slowly to about 140° F. as it passes over fresher bark. The temperature of the liquors can be controlled by having suitable heating coils placed in the tanks just under the false bottoms.

When a very hard, alkaline water is used in leaching, the tannin yield is sometimes low and the extract dark in color and of poor quality. This has been the subject of numerous investigations, from which the general conclusion has been drawn that the use of a soft water in leaching is imperative. But the work of Wilson and Kern seems to indicate that the question of hardness of the water used is of less importance than the pH value of water and liquor.

The commercial extract-manufacturing plants usually do their leaching of raw materials in autoclaves with rigid control of temperature, pressure, extraction rates, etc., and are equipped with vacuum concentrators and driers for producing either very concentrated liquid extracts or dry solids of high tannin content. Some plants develop a high degree of specializing on the manufacture of only one kind of extract, with which the individual tanner could hardly hope to compete.

Whether a tanner leaches any raw materials or not, he usually has a storage place for strong liquors, called a *leach house*. This contains wooden storage tanks, each with a capacity of more than 12,000 gals. and capable of receiving a tank-car of liquid extract at a time. In these huge tanks, solid extracts are dissolved in water and blends are made of various extracts and liquors that the tanner himself may have leached directly from raw materials.

In some localities, there is such a demand for leached oak bark that the tanner can readily sell the spent bark, after he has leached the tannin from it, for more than he paid for the original bark. In other localities, hemlock bark may be so cheap that it pays the tanner to leach it himself, even though he cannot produce liquors strong enough for his direct use, in which case he builds up the strength with purchased extracts. The control of the pH value of the liquors is tremendously important in vegetable tanning, and for this purpose many tanners purchase and leach raw myrobalans (nuts), divi-divi (pods) or valonia (cups and beards) and store the liquors until acid fermentation takes place, with formation of organic acids. When they wish to lower the pH values of the yard liquors, they increase the proportion of these liquors to the total stock liquor entering the yards; when they wish to raise the pH values, they decrease the proportion.



Fig. 165. A Barkometer.

Courtesy Chas. II. Stehling Co.

Use of the Barkometer

In the routine dilution of tanning extracts with water and in making up tan liquors, it is important to have some quick method for determining strengths of

liquors. If tan liquors are made up under uniform conditions, the tannin contents are roughly proportional to the specific gravities of the liquors for any one material.

A barkometer is a very simple form of hydrometer reading in barkometer degrees. One is shown in Fig. 165. For a specific gravity of exactly 1.000, it reads zero, and the barkometer reading is increased by 1° for each increase of 0.001 in specific gravity. For example, a barkometer reading of 45½° means a specific gravity of 1.0455. The specific gravity of a liquor changes with temperature and barkometer readings would give misleading results if the temperature of the liquor being tested were not taken into consideration. The standard temperature for recording barkometer readings is 60° F. If the temperature of the liquor is exactly 60° F., the reading is correct as taken. At higher temperatures, the readings will be low, and at lower temperatures they will be high. For example, suppose we had a tan liquor having a barkometer reading of 30° at 60° F. Raising the temperature of the liquor does not change its composition, but at 100° F. the barkometer reading would be only 24°, and at 40° F. it would be 32½°. However, it would be designated a liquor of 30° because that is the reading at 60° F. In order to avoid the necessity for bringing each liquor to exactly 60° F. before making the reading, Yocum devised the following table of corrections.

Table 26. Temperature Corrections for Barkometer Readings of Tan Liquors.

erved ling		At te	mpera	ture i	ndica obt	ted, ain	add the b	the fo	ollowii ieter	ng va readii	lues t	o the	obse F.	rved	readir	ng to	
Obs reac	40°	45°	50°	55°	60°	65°	70°	75°	80°	85°	90°	95°	100°	105°	110°	115°	120°
0	_	_	_	_	0	Į.	1	13	2	3	31	41	5	6	7	81	9
5	-2	-12	-1	-1	Ō	ā	1	11	2	3	34	43	5	6	7	83	9
10	-2	-12	-1	-12	0	ž	1	13	2	3	3½	44	51	63	71	81	93
15	-21	-12	-1	-12	0	3	1	12	24	3	32	4法	51	6₫	7å	83	93
20	-21	-12	-1	− ½	0	2	1	13	25	3	32	42	5₫	6₫	7≟	85	9≟
25	-21	13	-1	$-\frac{1}{2}$	0	2	1	13	23	31	32	43	5½	6월	73	83	93
30	$-2\frac{1}{2}$	-13	-1	-12	0	3	1	12	21	31	4	5	6	63	8	9	10
35	-21	-14	-1	-1	0	3	1	14	23	33	4	5	6	63	8	9	10
40	$-2\frac{1}{2}$	13	-1	1	0	2	1	13	2½	31	4	5	6	63	8	91	10
45	-2^{3}	-14	— 1 ,	-1	0	2	1	13	23	31	4	5	6	63	81	91	10
50	-23	-12	-1	-1	0	2	1	13	21	31	4	5	6	61	8.1	91	101
55	23	12	-1	-12	0	2	1	13	23	31	4	5	6	69	81	91	101
60	23	-12	-1	-2	0	7	1	13	2^{3}	31	4	5	6	64	81	91	101

Below 60° F., the minus sign (-) indicates that the number is to be subtracted from the observed reading to get the true reading at 60° F. Above 60° F., the number is to be added to the observed reading to get the true reading at 60° F.

The barkometer reading is a guide to tannin content only for pure solutions of the extracts, and the relation is different for each tanning material. Starting with one extract of which the tanner has the analysis, he should make up a solution of known strength and record its barkometer reading. Then by making successive dilutions and measuring the barkometer value for each dilution, he can make up a table of his own showing the relation of tannin strength to barkometer reading for pure solutions of this extract only. By repeating this for each extract that he uses, he can prepare a series of tables covering the relations for pure solutions.

For yard liquors, the barkometer reading includes everything in the liquor; thus the reading of a used liquor will be higher than that of a pure solution of the same tannin content. Whenever analyses of used liquors become available, the tanner should note the relation between tannin content and the barkometer reading. In this way, he can accumulate data that will make his barkometer readings valuable in indicating the tannin content. It must be remembered that the barkometer reading is merely a measure of the specific gravity of the solution, and will be increased by the addition of soluble matter other than tannin. It cannot take the place of a

tannin determination; but with sufficient accumulated data available it provides a very quick method of indicating the approximate strength of a liquor.

Bisulfiting

Ordinary solid quebracho extract contains insoluble matter that settles out in the form of a reddish brown sludge after the extract has been diluted with water and allowed to stand. Tanners have found that this insoluble matter can be rendered soluble by treating the extract with sodium bisulfite before making the final dilution. Moreover, this treatment with bisulfite causes the tannin to be taken up by the hides with greater avidity. A common method of bisulfiting quebracho extract in the leach house is as follows:

Tanks used for bisulfiting vary in size, but the procedure will be described for a cylindrical tank 9 feet in diameter by 7 feet deep. The tank is usually made of cypress wood and is equipped with copper coils for heating with steam and a horizontal revolving paddle, running at about 24 r. p. m. for mixing. Dump 10 tons of solid quebracho extract into the tank and cover with 2000 gals. of boiling water. Start the paddle revolving and apply heat as may be necessary to maintain a temperature of 180° F. When all the quebracho has dissolved and the liquor appears to be homogeneous, add 800 lbs. of sodium bisulfite dissolved in 500 gals. of water at 180° F. Run the paddle continuously, maintaining a temperature of 180° F. for 24 hours. Then cool and dilute to a strength of 25° Baumé, as measured with a Baumé hydrometer. It can then be stored for use in making up stock liquors for the tan yard.

The Baumé hydrometer is like a barkometer except for the range covered. Some tanners use a Twaddell hydrometer, which has a somewhat different range. Table 27 shows how to convert Baumé degrees into Twaddell degrees, barkometer degrees, or specific gravity.

Table 27. Conversion of Degrees Baumé into Degrees Twaddell, Degrees Barkometer and Specific Gravity at 60° F.

grees	Degrees Twaddell	Degrees Barkometer	Specific Gravity	Degrees Baumé	Degrees Twaddell	Degrees Barkometer	Specific Gravity
	0.0	0.0	1.0000	19	30.2	150.8	1.1508
ů.			1.0069	2 0	32.0	160.0	1.1600
Ţ	1.4	6.9			33.9	169.4	1.1694
2	2.8	14.0	1.0140	21		178.9	1.1789
3	4.2	21.1	1.0211	22	35.8		
4	5.7	28.4	1.0284	23	37.7	188.5	1.1885
5	7.1	35.7	1.0357	24	39.7	198.3	1.1983
6	8.6	43.2	1.0432	25	41.7	208.3	1.2083
7	10.1	50.7	1.0507	26	43.7	218.5	1.2185
8	11.7	58.4	1.0584	27	45.8	228.8	1.2288
0	13.2	66.2	1.0662	28	47.9	239.3	1.2393
9				29	50.0	250.0	1.2500
10	14.8	74.1	1.0741		52.2	260.9	1.2609
11	16.4	82.1	1.0821	30			1.2719
12	18.0	90.2	1.0902	31	54.4	271.9	
1.3	19.7	98.5	1.0985	32	56.6	283.2	1.2832
14	21.4	106.9	1.1069	33	58.9	294.6	1.2946
15	23.1	115.4	1.1154	34	61.3	306.3	1.3063
16	24.8	124.0	1.1240	35	63.6	318.2	1.3182
17	26.6	132.8	1.1328				
18	28.3	141.7	1.1417				
18	40.0	141./	1.171/				

The bisulfiting does more than merely dissolve the otherwise insoluble residue of quebracho extract; it also changes the character of the extract so that its tannins are taken up by the hide protein with greater avidity. It has a similar effect upon cutch extract, which has only an insignificant proportion of insoluble material. In the case of cutch extract, it also increases the rate of penetration of tannins into the thickness of the hides. Tanners using both quebracho and cutch in their yard blends often mix them and bisulfite them together.

The percentage of bisulfite used is based on the total solid content of the liquor;

it varies in different tanneries, but is usually between 3 and 5 percent of the total solids by weight.

Other solid extracts are usually dissolved like quebracho and stored as liquors of about 25° Baumé. Liquid extracts can be diluted with warm water much more readily than solid extracts.

Table 28. Tannin Contents by Official Method for Pure Solutions of Cutch, Chestnutwood, Quebracho (3% bisulfited), Chestnut-oak bark, and Hemlock-bark Extracts at Different Baumé Readings at 60° F.

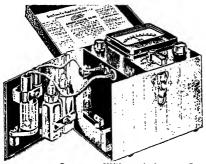
Degrees Extract Cutch Samme Extract Chestnut Wood Extract Chestnut Coak-bark Extract Chestnut Coak-bark Extract Chestnut Coak-bark Chestnut Chestnut	at Different	Daume Rea	idings at 00 1			
0	Degrees Baumé				Oak-bark	bark
1 1.4 1.2 1.6 2 2.8 2.3 3.2 3 4.1 3.5 4.9 4 5.5 4.6 6.5 5 6.9 5.8 8.1 6 8.3 6.9 9.7 7 9.7 8.1 11.3 8 11.0 9.2 13.0 9 12.4 10.4 14.6 10 13.8 11.5 16.2 11 15.2 12.7 17.6 12 16.6 13.8 19.0 13 17.9 14.9 20.4 14 19.3 16.0 21.8 15 20.7 17.2 23.2 16 22.1 18.3 24.6 17 23.5 19.4 26.0 18 24.8 20.6 27.4 19 26.2 21.7 28.8 20 27.6 22.8 30.2 21 28.9 24.0 32.9 22						
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33 37.3 34 38.3	32					
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	34				-	

Table 28 gives some information useful in operating the leach house on the relation of tannin content to Baumé up to 35° for pure solutions of cutch extract, chestnut-wood extract, 3 percent bisulfited quebracho extract, chestnut oak-bark extract and hemlock-bark extract. The values were calculated from data furnished by Mr. C. A. Blair on cutch, chestnut wood and quebracho, and by Mr. Charles Oberfell on chestnut oak bark and hemlock bark. In practice, the values vary with the purity of the extracts. The Baumé readings can be converted into Twaddell, barkometer and specific gravity readings by reference to Table 27. The operations of the leach house are described in greater detail in Chapter 11.

Electrometric Measurement of pH Value

The concept of pH value was described in Chapter 7, together with a very simple colorimetric method for determining it. The control of pH value is of vital importance in all tanning operations. Stock that will tan perfectly at one pH value may be completely destroyed at another. The colorimetric method cannot safely be used with vegetable tan liuors, and so it is necessary to use the more reliable and accurate electrometric method.

Although the electrometric determination of pH value by means of the glass electrode is very highly scientific and based on very involved theories of physical chemistry, modern instruments are so simple in their operation and so nearly foolproof that any previously inexperienced person can learn to make precision measurements almost at once, and a determination can be made in a very few minutes. Fig. 166 shows one of the simplest and cheapest (\$84.50) pH testers on the market. It covers the pH range 0 to 12 and is accurate to 0.1, which is accurate enough for most routine work in the tannery. It can be carried about the tannery to be used wherever needed.



Courtesy Wilkens-Anderson Co.

Fig. 166.

Glass-electrode Equipment for Determining pH Value in the Tannery.

The operation of the set is extremely simple. Although the box contains an electron tube, batteries and complex apparatus, the operator need not be concerned about this in making routine measurements.

A description of the routine involved in making pH measurements with this glass-electrode equipment will probably give the reader a better idea of the simplicity of making such measurements. In the face of the box and shielded by a window, there is a delicate needle pointer and a scale reading in pH values from 0 to 12. At one point on the scale, there is a red line marked by the letter S. Below the scale, there is a switch which can be set at 5 different points marked: BAL, READ, B, T and OFF. At the left of the scale, there is a dial knob marked AP and below the scale at the right is a dial knob marked BAL. On the left side of the case, there are two dial knobs, one marked T and the other T0. At the left side, there is a small beaker containing the glass electrode and the reference electrode. There are also two bottles, one with potassium-chloride solution and the other with a standard pH solution. Each bottle is equipped with a pipette for measuring and delivering the solution it contains.

Each morning the workman first calibrates his set as follows: He makes sure that the reference electrode is filled with potassium chloride solution and that there are no bubbles in the tube of the reference electrode. He pinches the rubber sleeve on this tube and allows a drop of potassium-chloride solution to escape so as to form a fresh surface of contact. After carefully cleaning the glass electrode and the beaker, he puts 2 pipettes of the standard pH solution into the beaker and fills to the halfway mark with distilled water, which gives him a solution of

fixed pH value of 4.1 against which to standardize the set. He then puts the beaker back in place so that the two electrodes dip into it, turns the switch to T, and allows several minutes for the set to warm up. Then he turns dial knob T to such point that the needle is exactly over the line S, after which he turns the switch to B and adjusts dial knob B until the needle is again exactly over the line S. After turning the switch to READ and adjusting dial knob BAL until the needle is again exactly over line S, he turns the switch to BAL and adjusts dial knob AP until the needle is again exactly over the line S. Upon turning the switch back to READ, the needle should remain over line S. The set is now ready for use.

Fill the beaker with the liquor whose pH value is to be measured and make sure the electrodes are in place in it. Turn switch to BAL and adjust dial knob BAL to bring the needle exactly over the line S. Then turn the switch to READ and read the pH value of the liquor directly from the scale.

Occasionally, adjust the T and B dial knobs as directed above, because this compensates for any variation in tube or battery. For each measurement, pinch the rubber sleeve of the reference electrode tube and allow a drop of potassium-chloride solution to escape in order to maintain a fresh liquid junction. Rinse the beaker and electrodes well with distilled water to keep them clean. Ordinarily, the set need be calibrated only once each morning, but can be recalibrated at any time as an extra precaution of safety.

This set can be carried about the tannery with safety. There are many different types of sets on the market, some of greater precision and higher price and all claiming some points of advantage over the others.

No attempt is made in this book to describe the principle of determining pH value with the glass electrode, because this book is written for tanners without any specialized knowledge of chemistry and physics. There are many books available that go deeply into the theory.

The Determination of Tannin

When a tanner buys 100 lbs. of tanning extract containing, according to the analysis, 25 percent of tannin, it is only natural that he should assume that he is really buying 25 lbs. of true tannin and that, upon using it in tanning, he can expect to find 25 lbs. of tannin in his leather; but such is not the case. In the case of materials containing such inorganic materials as iron, chromium, calcium, etc., he knows that he can rely upon an analysis with precision, but the tannins do not belong in this category. Commercial tanning materials consist of mixtures of substances so numerous and complex chemically that no one yet has been able to develop practical methods for their separation and evaluation. It was found, however, that useful methods could be developed to guard the tanner against adulteration and dilution in his purchases of tanning materials. One thing that a tanner desires to know about a tanning extract is how much of it will combine chemically with the hide and form leather that will remain stable against washing.

The official method of tannin analysis was based on the knowledge that hide powder can be used to remove tannin quantitatively from a tan liquor. It was a simple matter to determine the amount of soluble solids removed from a solution by hide powder and call it tannin. This method would have been accurate enough, if tannins were the only substances removed from solution by hide powder. Unfortunately, there are many substances that can be removed from solution by hide powder that are not tannins. This was not appreciated at the time of the acceptance of the official method. It is appreciated now; but the method, having been adopted to determine the price to be paid for certain commercial extracts, cannot be changed

lightly to some other method without a great deal of argument and discussion as to whether any new method might not later be found also to have flaws. In any event, it is very important for the tanner to know just what significance the determination of tannin has to him.

Since the official method sets conditions such that all true tannin is removed from solution, all values obtained give results that are higher than the true values by the amounts of nontannins removed from solution together with the tannins. Many tanning materials contain such substances as gallic acid, quinol, catechol, etc., which have no tanning properties and subsequently appear in the leather as part of the water-soluble material; but they combine loosely with hide powder and are removed from solution during the analysis and are thus included as tannin. If pure gallic acid, containing no tannin at all, is analyzed by the official method, it will show 46 percent tannin, simply because of the removal of gallic acid from solution by hide powder. The gallic acid can subsequently be removed from the hide powder by washing it with running water. The true tannins combine with hide protein so vigorously that they cannot be removed again by any practical amount of washing.

Wilson and Kern developed a method for determining the true-tannin content of vegetable tanning extracts by removing the tannins from solution quantitatively by shaking with hide powder and then analyzing the tanned hide powder for its combined tannin, as in the official method of leather analysis. The proportions of true tannin found by the Wilson-Kern method are always less than those found by the official method, as would be expected.

One sole-leather tanner kept a record over a long period of time of the total number of pounds of tannin entering his yards as determined by the official method, and also a record of the pounds of combined tannin in the leather produced. These records indicated that more than one-half of the tannin entering the yard was mysteriously lost in some way, until the Wilson-Kern method showed that no tannin was being lost at all, the apparent discrepancy in the records being due simply to the fact that the official method includes as tannin much material that merely forms a part of the water-soluble matter of the leather.

Table 29. Percentages of True Tannin in Various Tanning Extracts in Relation to Values Obtained by the Official Method of Tannin Analysis.

When official method shows 100 lbs. tannin in	Lbs, of true tannin present is
Mangrove bark (Cutch)	83
Quebracho wood	72
Wattle	72
Hemlock bark	61
Valonia	57
Chestnut wood	55
Spruce (Sulfite cellulose)	54
Oak bark	53
Myrobalans	49
Sumac	38
Gambier	31

Page carried this development a step further by differentiating between free water-soluble matter in leather and combined water-soluble matter. He called matter that could be removed from the leather with only small amounts of water the free water-solubles and matter that required more prolonged washing to remove it the combined water-solubles. The latter are bound to the hide in a loose combination like that of gallic acid in hide.

More recently Pound and Quinn have developed a method for evaluating in a

tanning extract the components that produce in leather (1) the free water-solubles, (2) the combined water-solubles, and (3) the fixed tannin. The fixed tannin is the same as the true tannin of Wilson and Kern. They showed that the official method includes as tannin the sum of the fixed tannin and the combined water-solubles.

In the large-scale production of vegetable-tanning extracts, the resulting products have become so uniform in composition that for each kind of extract the ratio of true tannin to material producing combined water-solubles is practically constant, although the ratio is different for different kinds of extracts. It seems inevitable that some day an official method like that proposed by Pound and Quinn will be adopted so as to give the tanner valuable information that he should have concerning the extracts that he buys. Meanwhile, Table 29 will serve him admirably, and his use of it will probably hasten the day when the official method will be changed to give him the same information on individual shipments.

The tanner will find this table very useful. For each 100 lbs. of official-method tannin in the form of mangrove bark that he puts in his yard, he can be assured of receiving 83 lbs. of combined tannin in his leather; and for each 100 lbs. of official-method tannin in the form of gambier that he puts in his yard, he will get only 31 lbs. of combined tannin in his leather.

Cost of Unit of True Tannin

Each kind of tanning extract confers upon the leather properties that are different from those produced by other kinds of extracts. In order to get the properties he desires in his leather, a tanner usually uses not one, but several different kinds of tanning extracts blended together. Two extracts having the same tannin content may produce very different kinds of leather. Nevertheless, it is very important to the tanner to know just what a tannin unit will cost him for each of the commonly used extracts. Prices are subject to change, but Table 30 gives a set of calculations based upon prices furnished to the writer in the summer of 1940.

Table 30. True-tannin Costs of Various Extracts (from quotations of July 1,	or july 1, 19th	Oı	quotations	(II OIII	Extracts	various	OI	Costs	ı rue-tannın	ie su.	\perp ar
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Extract	Official tannin (%)	True tannin (%)	Price per lb. (cents)	Price per lb true tannin (cents)
Spruce (liquid)	25	13.50	1.13	8.33
Mangrove bark (Cutch)	55	45.65	4.50	9.86
Quebracho wood (solid)	63	45.36	4.83	10.65
Wattle bark (solid)	60	43.20	4.95	11.46
Chestnut wood (liquid)	25	13.75	1.75	12.73
Valonia (powdered)	63	35.91	6.25	1 7.4 5
Hemlock bark (liquid)	25	15.25	3.00	19.67
Oak bark (liquid)	25	13.25	2.75	20.75
Myrobalans (powdered)	60	29.40	6.25	21.26
Sumac (Sicilian ground)	25	9.5 0	4.15*	43.68
Gambier (paste)	25	7.7 5	9.25	119.35

^{*} Quotation before Italy entered the war.

The cheapest tannin unit is contained in spruce (sulfite cellulose); but this material, when used as the only tanning material, does not impart the properties required for many kinds of leather. When the desired properties have been obtained by the use of mixtures of other types of vegetable-tanning materials, it is usually found that spruce tannin can be used to replace some of the more costly tannin units with no loss in quality of the leather. Although the gambier tannin unit is the highest priced, it has certain peculiar properties that warrant its use in

spite of its high cost. If it is desired to make heavy leather of enormous tensile strength, such as is required in linesmen's belts, the use of gambier is advantageous. It is also peculiarly valuable for certain very light leathers and as a mordant in dyeing leathers. Similarly, sumac is used largely as a mordant in the dyeing of leather and for very thin skins requiring considerable strength. In making sole leather, where the cost of the tannin unit is very important, the chief tanning materials are cutch, quebracho, wattle and chestnut, together with some spruce as a filler and myrobalans and valonia to furnish acid and provide the desired shade of color.

Relative Stability of Tanning Extracts

Paessler observed that tannin may be lost from liquors upon long standing, because of fermentation, oxidation, precipitation, etc. Table 31 gives the results he obtained from a series of liquors of 14° barkometer strength that were allowed to stand for 60 days.

Table 31. Tannin and Soluble-solids Losses in 14° Barkometer Liquors upon Standing for 60 Days.

m	—% loss after	
Tanning Material	tannin	solubl
Mangrove bark	0.0	0.0
Wattle bark	2.0	8.0
Sumac	1.5	8.0
Quebracho extract	4.0	6.5
Quebracho extract (bisulfited)	4.0	6.0
Õak bark	7.5	27.0
Chestnut-wood extract	11.5	8.0
Myrobalans	24.0	29.0
Valonia	29.0	30.0
Divi-divi	29.0	27.0

Seltzer and Marshall studied the tannin losses in a series of solutions of 0.4 percent tannin after intervals of 4, 8 and 12 weeks, and their results are given in Table 32.

Table 32. Tannin Losses from 0.4 Percent Tan Liquors after Standing Indicated Times.

	% tar	nnin loss after s	anding
Tanning Material	4 weeks	8 weeks	12 weeks
Mangrove bark (Cutch)	0.00	1.45	0.48
Wattle bark (raw)	0.81	2.75	2.91
Quebracho (heavily bisulfited)	0.72	1.29	4.32
Quebracho (lightly bisulfited)	1.36	3.41	6.13
Spruce (sulfite cellulose)	2.68	3.41	6.33
Hemlock bark extract (liquid)	0.40*	11.11	14.88
Chestnut-wood extract (liquid)	7.80	15.00	17.00
Oak-bark extract (liquid)	8.32	17.51	21.44
Valonia (raw)	15.38	23.54	27.51
Valonia extract (powdered)	25.70	35.26	40.04
Myrobalans (raw)	25.7 8	54.22	60.24

^{*} Represents gain.

In most sole-leather yards, the pH values of the liquors usually range from a high of 5.0 to a low of 3.0; the lower the pH value the greater the acidity. When the souring of yard liquors through acid fermentation gets out of control and becomes excessive, it is an old practice to save the hides from destruction by adding salt to the liquors. The destructive acid swelling of the hides can be prevented by

adding salt up to a maximum of 4 oz. per gallon. When acid is added to quebracho liquors, some of the tannins are precipitated and this precipitation is further increased by the addition of salt.

In a long series of tests, the writer studied the effects of pH value and of salt concentration upon the precipitation of tannins from liquors of different tanning materials. For each kind of tanning material, liquors were prepared having tannin contents of 1 and 6 percent. For each strength, liquors were acidified to pH values of 5, 4 and 3. For each pH value, salt was added to give concentrations of 0, 1, 2 and 4 percent. There were thus 24 different conditions for each tanning material. After standing for 24 hours, each sample was analyzed. The results for tannin losses are given in Table 33.

Table 33. Tannin Losses at Different pH Values and Different Salt Concentrations for Different Vegetable Tanning Materials.

No salt in liquors:	sta	cent of total nding for 4 tannin in liq pH=4	8 hours u	nder 24 di	r lost (-) fferent con annin in liq pH=4	ditions
Mangrove-bark extract (Cutch) Wattle bark (raw) Block mangrove bark (raw) Chestnut-wood extract Ouebracho-wood extract Oak-bark extract Hemlock-bark extract	+4	+4	+7	+3	+5	+6
	+1	0	-4	-1	0	0
	-2	-1	8	+1	+2	+1
	-6	-3	2	-8	-6	-3
	-12	-10	15	-3	-10	-11
	-6	-9	14	-11	-11	-20
	-7	-11	17	-14	-9	-21
1% salt in liquors: Mangrove-bark extract (Cutch) Wattle bark (raw) Block mangrove bark (raw) Chestnut-wood extract Quebracho-wood extract Oak-bark extract Hemlock-bark extract	-1	-3	-1	+1	+1	+3
	-10	-7	-10	-3	+3	-5
	-23	-9	-12	-3	-1	-3
	-27	-21	-19	-17	-18	-13
	-22	-21	-22	-22	-20	-25
	-27	-24	-29	-29	-24	-33
	-29	-29	-33	-35	-18	-33
2% salt in liquors: Mangrove-bark extract (Cutch) Wattle bark (raw) Block mangrove bark (raw) Chestnut-wood extract Quebracho-wood extract Oak-bark extract Hemlock-bark extract	9	-7	-6	-1	-2	+1
	15	-15	-8	-4	-8	-7
	9	-14	-13	-4	-3	-6
	35	-32	-31	-28	-23	-17
	33	-28	-30	-23	-27	-30
	36	-37	-37	-22	-37	-38
	35	-39	-41	-31	-37	-40
4% salt in liquors: Mangrove-bark extract (Cutch) Wattle bark (raw) Block mangrove bark (raw) Chestnut-wood extract Quebracho-wood extract Oak-bark extract Hemlock-bark extract	-15	-8	-23	-2	-4	-2
	-18	-12	-15	+1	-5	0
	-26	-20	-22	-10	-16	-13
	-60	-38	-33	-29	-26	-19
	-37	-38	-36	-29	-40	-43
	-49	-44	-50	-41	-45	-45
	-53	-54	-46	-47	-42	-47

Where no added salt was present, all the Cutch liquors showed a gain in tannin. In "The Chemistry of Leather Manufacture," page 439, the writer has described an interesting phenomenon in which certain non-tannins are converted into tannins. It may be that this phenomenon occurs under some conditions with Cutch and to a lesser degree with wattle bark to such an extent as more than to offset any tannin losses.

For each of the 7 tanning materials, tannin losses are given for 24 different conditions. The 24 values for each material were averaged and the results are given in Table 33. For simplicity in presentation, the values given in Table 33 were rounded out to the nearest whole number, but the averages in Table 34 were taken from the original data for greater accuracy.

In order to show how much of the tannin losses may have been due to precipita-

Table 34. Average Percentage of Total Tannin Lost from Tan Liquors Made From Different Materials under the 24 Conditions Described in Table 32.

Tanning material	% tannin lost
Mangrove-bark extract (Cutch)	0.3
Wattle bark (raw)	3.4
Block mangrove bark (raw)	6.0
Chestnut-wood extract	18.6
Quebracho-wood extract	23.7
Oak-bark extract	29.7
Hemlock-bark extract	31.4

tion, values for percentage insoluble in the 24 liquors of each tanning material were averaged and calculated as parts insoluble per 100 parts of tannin to make the results directly comparable with the tannin losses given in Table 34. These results, together with values for the original materials, are given in Table 35.

Table 35. Average Percentage Insoluble Matter on Tannin Basis Found in Tan Liquors Made from Different Materials under the 24 Conditions Described in Table 33.

Tanning material	original material	nsoluble on tans av. 24 liquors	nin basis———————————————————————————————————
Mangrove-bark extract (Cutch)	3.1	1.4	- 17
Wattle bark (raw)	2.5	2.6	- 0.1
Block mangrove bark (raw)	4.0	6.3	- 2.3
Chestnut-wood extract	2.0	11.1	- 9.1
Quebracho-wood extract	11.1	17 4	-6.3
Oak-bark extract	18.9	48.6	-29.7
Hemlock-bark extract	25.1	35.4	-10.3

Under the conditions of the tests, more than one-half of the insoluble matter of the Cutch extract passed into solution, which may account for some of the gains in tannin found. The fact that the Cutch mangrove grows in salt marshes may have something to do with its remarkable stability in the presence of salt. Cutch extract contains 2.0 percent of sodium chloride and 1.2 percent of magnesium chloride by weight. Precipitations of chestnut, quebracho and hemlock account for less than one-half of the tannin losses. It may be merely a coincidence that the precipitation loss of oak is exactly the same as the tannin loss.

Cutch is the most stable of all the tanning materials tested, with wattle a close second. Hemlock and oak barks, once the most widely used, are least stable and they have become rather expensive per unit of true tannin.

Relative Fixation Values of Tanning Materials

When applied to leather, the terms combined tannin and fixed tannin mean exactly the same thing, namely, organic matter combined chemically with the hide protein so vigorously that it cannot be removed by washing with water in any reasonable length of time. Gallic acid and certain other non-tannins combine readily with hide, but they can be removed by prolonged washing with water. If they combined so vigorously that they could not be removed by washing, they would be classed as tannins. In order to differentiate between the loose combinations of non-tannins and the vigorous combinations of the true tannins, the term fixation has been applied to the vigorous combinations.

In tannery practice, when hides are put into a tan liquor, they do not remove *all* the tannin from the liquor in any reasonable length of time, even when they have the capacity to combine with much more tannin than is present in the liquor. For this reason, as well as to mellow and condition the liquors, tanners use *press*-

over systems, using the same liquor for successive lots of hides until its tannin content is nearly exhausted.

For the same set of conditions, the *rate* at which the tannins become fixed by the hides varies greatly for different tanning materials. For example, if two series of tan liquors are made up with identical tannin contents, one series with cutch extract and the other with quebracho extract, and the same quantity of hides is passed through each series until all the hides are completely penetrated, and if then all the hides are taken out after having been in the liquors the same length of time, the hides from the cutch liquors will be found to contain more than twice as much fixed tannin as those from the quebracho liquors, even though the quebracho penetrates the hides much more rapidly than the cutch does. If the hides from the quebracho liquors are put back into their respective liquors and left for a longer time, they will still not take up as much tannin as the hides in the cutch liquors did in a much shorter time. Hides have a much greater avidity for cutch tannin than they have for quebracho tannin. As a measure of this avidity, we determine the number of pounds of tannin combined with 100 lbs. of hide protein under a given set of conditions and call it the *relative fixation value*.

The significance of this important property of tanning materials will be made clearer by the following description of a series of experiments run to determine the relative fixation values of different tanning materials and mixtures thereof. An ex-light steer hide was put through the beamhouse and treated in the manner generally approved for sole leather. Rectangular pieces were cut from the butt area in such manner as to give representative and comparable samples. These were suspended in the tan liquors contained in flat battery jars having width and depth slightly greater than the width and length of the hide pieces, corresponding roughly to the proportions commonly found in rocker vats in the tannery. Each piece was suspended first in a tan liquor of 0.5 percent tannin and left for 2 days. The liquor was then run away and replaced by a fresh one of 1 percent tannin. In this manner, the strengths of the liquors were increased by 0.5 percent tannin every other working day until a strength of 6 percent tannin was reached. The piece was then left in this liquor until the total tanning time was 42 days. It was then taken out, oiled lightly to prevent oxidation, dried slowly and analyzed. One piece of hide was taken for each kind of tanning liquor.

The tanning time of 42 days was considered sufficient for comparative purposes, since it allowed 9 days' contact of hide and liquor after even the slowest penetration was completed. The bisulfited quebracho was made from the ordinary quebracho extract by bisulfiting with 3 percent by weight of sodium bisulfite.

Table 36 gives a list of the different tanning materials used, their mixtures, the days required for complete penetration through the thickness of each piece, the pH value of the final used liquor, and the fixed tannin in the leather in terms of lbs. of tannin combined with 100 lbs. of hide protein.

For this specific set of conditions, the value for fixed tannin is a measure of the fixation value of the given extract or mixture. It will be noted that the fixation value for bisulfited quebracho is much higher than that for ordinary quebracho. In other words, bisulfiting quebracho so changes the nature of its tannins that hide protein combines with it with much greater avidity.

This table is of tremendous value to the sole-leather tanner and should be studied by him with minute care. It should be remembered that the stock tanned was an ex-light steer hide where the effects of rate of penetration are much less than with heavy steer hides. pH value plays a very important part in both tannin combination and in rate of penetration; the pH values were measured, but no

adjustments were made purposely, so that the pH values produced naturally by the different extracts could be observed. Decreasing the pH value generally causes an increase in fixation value, but a decrease in rate of penetration. If the tanning time is limited, a low rate of penetration may result in a lesser total fixation of tannin because of the short time of contact of the tannin with the middle layer of the hide.

Table 36. Lbs. of Tannin Combined with 100 Lbs. of the Hide Protein of an Ex-light Steer Hide in 42 Days, the Final pH Values of the Liquors and the Number of Days Required for Complete Penetration of Hide by Tannin.

Tanned with equal parts on tannin basis of	Fixed tannin	Final pH value	Days to penetrate
	69.61	4.37	16
1. Cutch extract alone			
2. Chestnut-wood extract alone	64.55	3.20	14
3. Cutch-Chestnut-Bisulfited Quebracho	52.66	3.50	14
4. Cutch-Bisulfited Quebracho-Spruce	49.25	3.42	22
5. Hemlock-bark extract alone	46.48	4.28	19
6. Cutch-Wattle-Spruce	45.51	3.60	27
7. Cutch-Chestnut-Wattle	44.83	3.67	16
8. Oak-bark extract alone	44.04	4.55	30
9. Cutch-Quebracho	43.21	4.33	25
10. Cutch-Chestnut-Quebracho	42.44	3.62	1 <i>7</i>
11. Bisulfited Ouebracho alone	40.47	6.07	10
12. Cutch-Wattle	40.30	4.37	18
13. Chestnut-Wattle-Bisulfited Quebracho	39.92	3.53	14
14. Valonia alone	37.61	3.83	20
15. Wattle-bark extract alone	37.15	4.76	11
16. Chestnut-Wattle-Quebracho	37.10	3.67	10
17. Cutch-Wattle-Bisulfited Quebracho	36.29	4.42	14
18. Wattle-Bisulfited Quebracho-Spruce	34,44	3.57	20
19. Quebracho-wood extract alone	29,63	5.27	18
	27.45	3.13	
20. Myrobalans extract alone	47.45	3.13	33

Cutch extract has by far the highest fixation value, and the writer has found that the yield of sole leather produced by any blend of tanning materials can be increased by increasing the proportion of cutch in the mixture. Myrobalans extract had the lowest fixation value, but its liquor had the lowest pH value, which causes an increase in the time required for penetration. Myrobalans is not used primarily for its tannin content but as an acid producer, and the low pH value of its liquor proves its efficiency in this regard.

Ordinary quebracho extract has a relatively poor fixation value and low rate of penetration, but bisulfiting increases its fixation value by more than 36 percent and its rate of penetration to the speediest of all.

Chestnut is second in fixation value and penetrates more rapidly than cutch alone. The part played by spruce extract is interesting; when used to replace chestnut in mixture with cutch and wattle, it produces a slightly increased fixation value, but greatly decreases the rate of penetration. When used to replace cutch in mixture with wattle and bisulfited quebracho, it decreases both the fixation value and the rate of penetration. Because of its effect in slowing the rate of penetration, spruce is used largely after the preliminary tanning in order to increase the weights and gains of sole leather.

Many tanners will be interested in knowing the results of combinations and conditions not shown in Table 36. It should be pointed out that any tanner with a chemical laboratory at his disposal can obtain similar results for any materials, combinations and sets of conditions that he desires by following the procedure outlined. Many tanners who have not previously thought of doing work of this kind

for their own special information will find it extremely valuable in helping to operate their tanneries at highest efficiency.

Of the results of blends shown in Table 36, the most promising is that start and equal mixture on tannin basis of cutch, chestnut and bisulfited quebracho. It may be significant that these three materials represent the first three in order of quantity used in the United States. The writer has operated sole-leather yards with this mixture and has obtained excellent results in quality, plumpness, solidity and yield of leather. The yields of leather were well above average and the cost below; and the leather gained a reputation for its unusual fineness of quality. By leaving the proportion of chestnut constant at one-third on tannin basis, the writer found that he could increase the rate of penetration of tannin into the hides at will by increasing the proportion of bisulfited quebracho to cutch, and that he could increase the plumpness and yield of leather and lower the cost of tanning materials by increasing the proportion of cutch to bisulfited quebracho. This is in full agreement with the data given above and shows that they are borne out in practice.

Most tanners know that hides remove tannins from liquors with increasing avidity when increasing amounts of acid are added to the liquors. In the experiments described above, no acid was added to any liquor, but the pH values show that the acidities of the different liquors differed widely because of the different natures of the various tanning materials. In order to show the effect of pH value upon the fixation value, five experiments were run with the cutch-chestnut-bisulfited quebracho mixture, each at a different pH value.

In these experiments, a light steer hide was used. As it was heavier than the ex-light steer hide used in the earlier experiments, a longer time was required for penetration. The experiment was run exactly like the earlier one except for control of pH value. Lactic acid was used to lower the pH values. The pH values chosen were 5.0, 4.5, 4.0, 3.5 and 3.0, which represents the extreme range found in most tanneries. When liquors with pH values as low as 3.0 are used, special precautions must be taken to prevent acid swelling and consequent destruction of the hide. The tanning of each piece was started in a liquor of pH value 2.0 higher than the pH value at which most of the tanning was to be done. For example, the piece to be tanned at a pH value of 3.0 was started at a pH value of 5.0 and this was lowered gradually to 3.0 in the course of 7 days, by which time penetration had progressed far enough to prevent damage when the pH value was lowered to 3.0. The total tanning time was 42 days, as in the previous experiments and so each piece was in liquor at the indicated pH value for 35 days after having been in liquors of higher pH value for 7 days.

The results are shown in Table 37.

Table 37. Effect of pH Value upon Lbs. Tannin Combined with 100 Lbs. Hide Protein of Light Steer Hide in 42 Days and Number of Days Required for Tannin to Penetrate the Hide Completely, Using Equal Parts on Tannin Basis of Cutch, Chestnut and Bisulfited Quebracho and with Tannin Strengths Increasing Gradually from 0.5 to 6.0 percent.

Final pH Value	Fixed tannin	Days to penetrate
5.0	37.3	19
4.5	42.2	19
4.0	43.0	24
3.5	50.6	24
3.0	56.8	42

With pH value decreasing from 5.0 to 3.0 by the addition of lactic acid, the fixation value rises from 37.3 to 56.8 and the time required for the tannin to

penetrate completely through the hides increases from 19 to 42 days. In Table 36, results for the same mixture on a lighter hide gave a fixation value of 52.66 and a penetration time of 14 days at a pH value of 3.5. The results in Table 36 for a pH value of 3.5 show that the effect of greater thickness in the hide was to increase the time required for complete penetration from 14 to 24 days and to lower the fixation value from 52.7 to 50.6, using the same total time in the liquors.

A small increase in thickness of a hide requires a relatively large increase in time to effect complete penetration by tannin. If the tanning time is kept constant and thicker hides are used, there will be corresponding decreases in fixation values because of the shorter time of contact of the tannins with the middle layers of the hides. When very heavy hides are tanned, the differences in time required for different tanning materials to penetrate them become very great.

A series of experiments was run with a very heavy steer hide exactly like those whose results are given in Table 36 except for the tanning materials used and the extension of the tanning time to 57 days. In one experiment the cutch was bisulfited like the quebracho. The results are shown in Table 38.

Table 38. Lbs. Tannin Combined with 100 Lbs. Hide Protein of a Heavy Steer Hide in 57 Days, the Final pH Values of the Liquors and the Number of Days Required for Tannin to Penetrate the Hide Completely.

	Fixed	Final	Days to
Tanned with parts on tannin basis of	tannin	pH value	penetrate
•		-	-
Bisulfited Cutch extract alone	47.01	4.19	5 <i>7</i>
Cutch extract alone	38.36*	3.81	over 57
Chestnut-wood extract alone	38.72	2.94	37
Bisulfited Quebracho alone	28.42	4.10	17
Wattle-bark extract alone	28.30	4.10	18 50
50% Cutch-50% Chestnut	43.68	3.22	5 0
50% Cutch-50% Bisulfited Quebracho	37.49	3.71	23
50% Chestnut-50% Bisulfited Quebracho	32.84	3.15	21
25% Cutch-37½% Chestnut-37½% Bis. Quebracho	36.84	3.30	23
50% Cutch-25% Chestnut-25% Bis. Quebracho	43.47	3.02	27
75% Cutch-12½% Chestnut-12½% Bis. Quebracho	46.92	3.54	37

^{*} This value cannot be used as a fixation value because the hide still had a raw streak in it at the time it was taken out for analysis.

For very heavy hides like this, it would be impractical to use cutch extract alone because of the very great length of time required to get the tannin to penetrate completely through the stock. It would be impractical to use bisulfited quebracho alone because of the low fixation value, which results in flat leather of low yield. The use of chestnut alone is not desirable because of the color of the leather, its low resistance to decomposition by acids, the long time required for penetration and other characteristics not readily described, but which a tanner gets to know through experience.

Equal parts of chestnut and quebracho give a satisfactory penetration time, but the yield is low. Equal parts of chestnut and cutch give a very satisfactory yield, but the penetration time is too long. Equal parts of quebracho and cutch give satisfactory yield and penetration time; but an improvement in yield is obtained by replacing some of the quebracho by chestnut, with but little increase in penetration time. With each increase in cutch, there is an increase in yield of leather, accompanied by an increase in penetration time. All this explains why tanners rarely use only one vegetable tanning material; they use mixtures, so that the advantages of one will offset the disadvantages of another. A good blend will produce far better leather than any one material used alone. Color

is an important property in vegetable-tanned leather, and sometimes a tanner will pay a premium for a material that will impart to the leather the shade and kind of color that is pleasing to the consumer. In arriving at a suitable blend, he must take into consideration the cost of the materials based on their true tannin contents, their stabilities, their properties in use and the properties which they impart to the leather.

Effect of pH Value on Color of Tannins

Vegetable-tanning materials change in color with change of the pH value of their solutions, resembling in this respect the indicator dyes used with the La Motte Comparator for determining pH value. When vegetable-tanning materials are analyzed, it is customary to tan a small piece of sheep skiver to show the color which the tanning material imparts to leather. The color obtained is meaningless unless the pH value is defined, because the color is different for each pH value. At a pH value of 3.0, most tanning materials have very light colors. With increasing pH value, the color deepens. For example, the color of a gambier liquor at a pH value of 3.0 is light straw, which gradually turns to a dark red as the pH value is raised to 12.0. Over the same range, quebracho liquors change from a light pink to a deep red with a violet tinge. The change in color is reversible and can be made light or dark at will by lowering or raising the pH value.

Use is made of this principle in bleaching sole leather. After the leather has been tanned it is immersed in a solution of soda ash (sodium carbonate) to cleanse the grain, and then in a solution of sulfuric acid to lighten the color.

Effect of pH Value on Oxidation of Tannins

When vegetable-tanned leather is hung to dry, if the drying is done rapidly in a current of warm air, the leather becomes badly discolored by deep red to purple stains; washing in an alkaline solution followed by an acid bleach may be necessary to remove them. This is caused by a chemical reaction between the tannins and oxygen from the air. The compound of tannin and oxygen is no longer a true tannin, but a resinous material insoluble in acidified water, but soluble in alkaline solutions. This kind of oxidation is apparently responsible for some of the tannin losses that occur when some kinds of tan liquors are allowed to stand for a long time exposed to air.

Wilson and Kern developed a method for measuring the extent of this oxidation in tan liquors by allowing the oxidation to take place and then acidifying the liquors to a pH value of 3.0, at which the oxidized tannins are precipitated and can be measured. They found that oxidation proceeds at the greatest rate when the pH value of the liquor is about 9. They set up two series of liquors containing 1 percent of tannin, one of gambier and the other of quebracho, and adjusted the pH values of each series over a range from 3.0 to 12.0. They allowed all liquors to stand in shallow dishes exposed to air for 3 days. They then added hydrochloric acid to each liquor to bring its pH value to 3.0. The liquors were placed in 100-cc. graduated cylinders; the precipitates of oxidized tannin were allowed to settle, and their volumes were measured. The results are shown in Fig. 167.

Little or no oxidation of gambier takes place at pH values below 5.0, but some oxidation of quebracho appears to take place at all pH values down to 3.0. Above a pH value of 5.0, oxidation of both materials takes place with accelerating rapidity up to a pH value of 9.0. Some tan yards are operated on such basis that the lime in the stock entering the tail liquors has a tendency to raise the pH value above 5.0. When this occurs, the stock becomes discolored by the oxidizing tan-

nins; if the pH value is allowed to rise as high as 7.0, putrefaction of the stock also sets in and the damage to the stock becomes irreparable. It has been the writer's privilege to save more than one tanner from ruin by teaching him to add acid to the tail liquors whenever the pH value rose above 5.0.

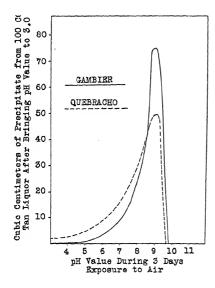


Fig. 167.

How Oxidation of Tannins Proceeds at Different pH Values as Determined by Acidifying to pH Value of 3.0 after Oxidation Has Taken Place and Measuring Volume of Precipitate.

Effect of pH Value on the Precipitation of Quebracho Liquors

As was shown in Table 33, considerable tannin losses occur in quebracho liquors when acidified to pH values below 5.0. Wilson and Kern also studied the effect of pH value on the precipitation of quebracho liquors. They used liquors of 0.4 percent tannin and sulfuric or hydrochloric acid to lower the pH value, and lime or caustic soda to raise it. The results are shown in Fig. 168.

The solution receiving no addition of acid or alkali had a pH value of 4.60. As the pH value was lowered from this by the addition of either acid, there was an increase in the percentage of insoluble matter found by analysis, sulfuric acid proving the more effective in causing precipitation. With increasing pH value, there was first a decrease in the percentage of insoluble matter found, and the unfiltered solutions gradually became more nearly transparent. In the case of the liquors treated with caustic soda, this continued without a break, the liquor having a pH value of 11.35 being quite transparent. Where lime was used to raise the pH value, the insoluble matter continued to pass into solution until a pH value of 7 was reached, above which the tannin was precipitated in increasing amounts.

These results suggest that the insoluble matter in quebracho extract consists at least partially of oxidized tannins, which we know are soluble in alkaline solution, and is precipitated in increasing quantity as the pH value is lowered. They also suggest a parallel between the bisulfiting of quebracho extract and the production of spruce extract. The lignins of spruce wood are insoluble in water, but can be dissolved by treatment with alkali or with lime and sulfur dioxide. In this respect, they behave like oxidized tannins and may actually be essentially the same. After the treatment of the wood lignins with lime and sulfur dioxide,

which corresponds to bisulfiting, they become soluble in acid solution and have tanning properties. If the results of mixtures No. 6 and 7 in Table 36 are studied, it will be observed that spruce extract adds as much fixation value to the mixture as does chestnut extract, which has a much higher fixation value than quebracho extract. If the bisulfiting of the oxidized tannins of quebracho is similar in principle to the bisulfiting of spruce lignins, it is readily understood why bisulfiting quebracho decreases the insolubles and increases the fixation value.

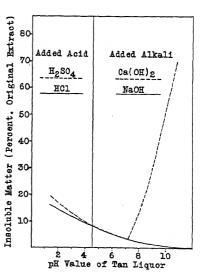
The precipitation of quebracho by lime at pH values above 7 furnishes another powerful reason for guarding the tail liquors against undue rises in pH value.

Acid Fermentation in Tan Liquors

In the simple fermentation of sugars by yeasts, about one-half of the weight of the sugars becomes carbon dioxide gas and the other one-half becomes alcohol. The alcohol becomes oxidized to acetic acid, when the liquor is exposed to air, as in the case of the souring of wines. In tan liquors, fermentation is greatly complicated by the presence of molds and other microörganisms which secrete enzymes that break down, or hydrolyze, the tannins of some kinds of tanning materials. For example, the common black mold, *Aspergillus niger*, secretes the enzyme tannase, which breaks down the tannins of chestnut wood, myrobalans and other tannins of the pyrogallol type, and one of the end-products is gallic acid. This type of acid

Fig. 168.

Effect of pH Value on the Precipitation of Quebracho Liquors by Sulfuric Acid (H₂SO₄), Hydrochloric Acid (HCl), Lime (Ca(OH)₂) and Caustic Soda (NaOH).



fermentation has been known to ruin tanners who were not familiar with it. Not only is tannin destroyed, but excessive amounts of acid in the liquors cause an acid swelling and destruction of the stock. With the advent of pH control and the knowledge of how to use salt to prevent destructive acid swelling, this danger has been practically eliminated.

Cameron and McLaughlin developed a method for determining the contents of lactic, acetic and gallic acids in vegetable-tanning extracts and obtained results for cutch, oak, hemlock and chestnut. Using their method the writer obtained results for wattle, quebracho and myrobalans extracts. The results, calculated to dry basis, are given in Table 39.

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Extract	Lactic acid %	Gallic acid %	Acetic acid %	Sugars %	pH value
Chestnut	0.14	12.03	0.79	11.61	3.29
Myrobalans	0.70	9.14	0.04	10.27	3.28
Oak	0.60	3.59	0.20	13.09	4.37
Hemlock	0.34	2.05	0.16	11.27	3.77
Cutch	1.20	0.10	0.13	1.92	4.12
Quebracho	0.05	0.80	0.18	1.58	4.64
Wattle	0.005	0.32	0.02	5.39	5.03

Table 39. Acid and Sugar Contents of Vegetable-tanning Extracts and pH Value of Solutions of 0.4 percent Tannin.

The order given is for decreasing total acid content. Chestnut-wood extract not only has the highest acid content, but most of the acid present is gallic, which is probably formed as a by-product of destruction of tannin. This extract also has the highest sugar content, and sugar also would be a by-product in the destruction of tannins of the nature of penta-digalloyl-glucose. The gallic acid would also be responsible to some extent for making the tannin determination by the official method higher than the true value. Cutch has the highest content of lactic acid, but its total acid content is relatively low. Wattle has the least total acid.

The four extracts containing the highest total percentages of acids have most of their acid present as gallic; these are relatively unstable in dilute solution upon long standing. It should be noted that these extracts were not allowed to ferment appreciably after manufacture and that fermentation would be greatly accelerated after dilution. Quebracho has very little total acid, but its dilute solutions are relatively unstable. In this case, it seems probable that tannin losses on standing are due to oxidation. Cutch and wattle are extremely stable.

Discoloration of Tannins by Iron

Vegetable tannins combine vigorously with iron compounds, forming products of very intense blue-black color. So intense is this color that iron compounds of the tannins are widely used in the preparation of black inks. Exceedingly small percentages of iron present in extracts give them an intense blue-black color; therefore the presence of iron must be avoided as far as possible, if leather of light color is to be made.

Tanners must avoid contact of their extracts and liquors with iron. Storage tanks are usually made of cypress wood, and conduits of copper. Discolorations by small proportions of iron can be eliminated by the addition of Calgon (polymeric sodium metaphosphate) to the liquors. This combines more vigorously with the iron than do the tannins, with the formation of a light-colored or colorless product.

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Chapter 11

Vegetable Tanning

Raw skin is readily putrescible in the wet state. Upon drying, the collagen fibers become glued together and the skin becomes very stiff. Although the dried skin will not putrefy, it again becomes putrescible as soon as it comes into contact with water. Thousands of years ago the discovery was made that the properties of skin substance change completely when the wet skin is brought into contact with the aqueous extract of those forms of plant life which have since come to be classed as vegetable tanning materials. The action which brings about this change of properties is known as vegetable tanning, and the compound of skin protein and tannin as leather. Under normal conditions, the fibers of leather do not glue together upon drying and they are not putrescible even in the wet state.

The practice of tanning is greatly complicated by the necessity for imparting to the leather many delicate properties, according to the use to which it is to be put, all of which are markedly affected by slight differences in manipulation. The effect produced by any single change in the tanning process depends upon the nature of every one of the numerous operations preceding and following that in which the change has been made. In the manufacture of one type of leather, a skin may be subjected to scores of different operations, and a slight change in any one of these may necessitate changes in nearly all the others in order to preserve the specific properties desired in the finished leather. It is this fact that renders most practical treatises on leather manufacture of so little value to the tanner. Were he to try to adopt an operation described in the literature which was better in itself than the one he was using, he might find that the change would spoil his leather because of its failure to harmonize with all the other operations peculiar to his particular process.

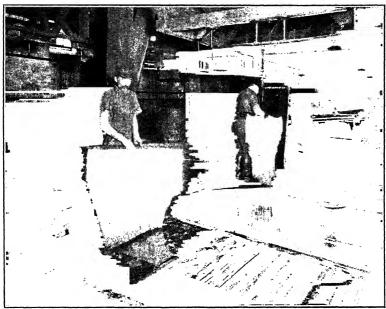
To avoid this difficulty, the writer has tried to provide in this book, a continuity of procedures, each specific in itself. Many writers who describe procedures avoid specific details because they realize that the conditions best for one tanner may not be best for another, and that variations in types of raw stock require corresponding variations in procedure to get the best results. When the latitude given in procedures is too wide, the tanner may be at a loss to know just how to proceed unless advised by someone with previous experience on the type of stock he is using. For any single test, a specific procedure must be outlined. After the results are known, an opportunity is afforded to make such changes in procedure as may be necessary to alter the properties of the leather in the direction desired.

From many years of experience in developing new procedures and in introducing procedures into a tannery for the first time, the writer has found it essential to prepare the procedure in specific detail and then to indicate how to improve upon the results, once they are known. In Chapters 7, 8 and 9, very specific procedures were described for handling green, salted calfskins through the bating and pickling operations. These will produce reasonably satisfactory results for any kind of green, salted calfskins. This provides continuity of procedure. It was then shown how the details could be varied, depending upon the results, to make improvements.

The writer has found this method of presentation eminently satisfactory in many different tanneries.

Vegetable Tanning Bated Calfskins

In Chapter 9 specific details were given for bating calfskins and for pickling them after bating. Under some conditions, it is preferable to vegetable-tan calfskins directly after bating, without pickling at all; under other conditions, it is preferable to pickle them before tanning. Since the tanning conditions are of necessity different in the two cases, it is necessary to describe them separately.



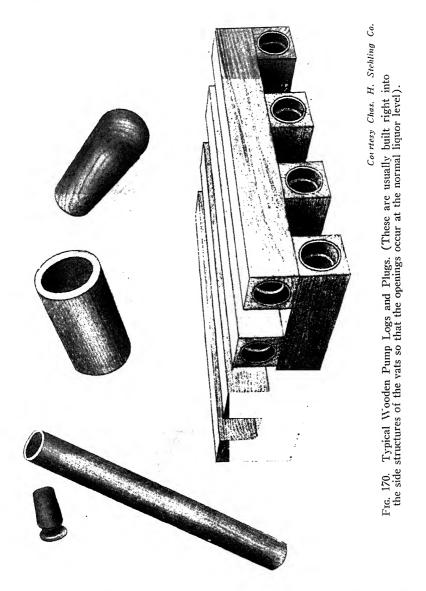
Courtesy A. F. Gallun & Sons Corp.

Fig. 169. Hanging Bated Calfskins in Vegetable Tan Liquors.

When bated stock is put into a tan liquor, any violent mechanical agitation must be avoided in order to prevent a severe grainy condition of the stock, which becomes set by the tannage. It is customary to start the tannage by suspending the skins, tacked to sticks, in still vats of tan liquor. The method of tacking bated calfskins to the sticks is shown in Fig. 169. In the background the tackers may be seen at work. Each skin is laid out flat on a table and tacked to a wooden stick with 5 heavy copper tacks so that the skin will hang head down when suspended from the stick. In the foreground may be seen a man immersing the skins in a tan liquor in a still vat. He is very careful to have the skin smooth and free from wrinkles when he puts it into the liquor. When the skin is completely submerged, the stick rests on a wooden frame and the skin hangs head down in the liquor.

The tan yard is divided into sections of wooden vats, 6 feet deep, with their tops flush with the floor level. Each section is about 70 feet long by about 10 feet wide and is divided into 6 stick vats, each 10 feet square, and 4 handler vats, each 5 feet square. All vats in any one section are connected by means of a pump

log, a wooden conduit, with openings into each vat about 6 inches below the top. These openings are normally closed by means of wooden plugs. Typical pump log structures are shown in Fig. 170. If the liquor level of any one vat in the



section is below the pump-log entry and that of another is above it, when the wooden plugs of both vats are removed, liquor will flow from the vat of higher level to the vat of lower level until the one of higher level is filled just to the pump-log entry. In this way, overflows from any one vat can be run into any other vat in

the section that is not filled to the pump-log entry. Each vat is also equipped with bottom outlet for draining to sewer when necessary.

Each stick vat is provided with two floating wooden frames, each about 9 ft., 10 in. long by about 4 ft., 10 in. wide. These frames support the wooden sticks to which the skins are tacked. Each stick is 4 ft., 10 in. long by about 1 sq. in. cross-section. Each stick vat has a capacity of about 150 calfskins. In each section, one stick vat and one handler vat is used to receive overflow liquor from the vats in use. The bated stock passes successively through 5 stick vats and 3 handler vats, remaining for one working day in each.

The number of different mixtures of tanning materials that can be used to produce satisfactory leather is very great. However, the writer has selected a mixture of three on the basis of low cost and fineness of quality of the finished leather. These are solid cutch extract, ordinary solid quebracho extract and liquid spruce extract. Chestnut-wood extract and myrobalans are not suitable for calf upper leather because of the *bloom* of ellagic acid which they deposit on the grain surface of the leather. Gambier is a good material to use, but its cost is too high.

The quebracho is dissolved separately from the others. A thousand lbs. of ordinary solid quebracho extract is placed in a wooden storage tank equipped with a copper coil for heating with steam. Enough boiling water is added to produce a final volume of 1000 gals. After all the quebracho has dissolved, the liquor is agitated by any suitable air blow to mix it thoroughly, and it is then pumped to a settling tank, where it is allowed to cool over night. Next day, it will be found that the insoluble matter has settled out on the bottom of the tank as a sludge. The clear liquor is decanted off from the settled sludge and pumped into the storage tank. Into another tank is placed 400 lbs. of solid cutch extract and 1000 lbs. of liquid spruce extract. It is covered with 500 gals. of boiling water and mixed well until completely dissolved. Then 380 gals. of the decanted quebracho liquor is added, the liquor is diluted to a total volume of 1500 gals., mixed well and cooled for use. The dilution should be such that, after the liquor is cooled, 1500 gals. contains 380 lbs. of solid quebracho (minus its insolubles), 400 lbs. of cutch and 1000 lbs. of spruce. This constitutes the *stock liquor* for the yard.

Give each vat in any section a permanent letter according to its physical position in the section. For example, in section No. 1, call the first stick vat A, the second B, etc., and the sixth one F. Then label the first handler vat G, etc., and the fourth one J. Designate each vat also by a temporary number according to its order in the series through which the bated skins pass, which will change from one cleaning period to another. When starting a section fresh, label the six stick vats in order, A-1, B-2, C-3, D-4, E-5 and F-0, the θ for the sixth stick vat indicating that it receives the overflow liquor for the period. The bated stock always goes first into No. 1, then into No. 2, etc. in order through No. 5, and then into the handler vats, which will be labelled G-1, H-2, I-3 and J-0, the fourth handler vat receiving the overflow liquor for the period.

In starting a section for the first time, add 400 gals. of stock liquor to A-1, 640 gals. to B-2, 880 gals. to C-3, 1120 gals. to D-4 and 1280 gals. to E-5. Leave vat F-0 empty to receive the overflows from the other stick vats during the strengthening of the liquors. To handler vat G-1, add 360 gals., to H-2 400 gals., and to I-3 440 gals. Leave J-0 empty to receive overflow liquor. Then fill each vat receiving stock liquor with water at 70° F. to the overflow plug and mix thoroughly. This is best done with compressed air passed through a half-inch copper pipe about 7 feet long, attached to the compressed-air line by means of

a flexible hose. To mix the liquor thoroughly, it is merely necessary to pass the outlet opening of the copper pipe along and across the bottom of the vat while the air is turned on. If compressed air is not available, the liquor can be mixed by means of a wooden plunger operated by hand. The general starting arrangement of the vats is shown in Fig. 171.

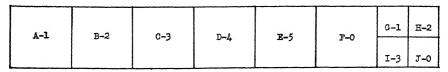


Fig. 171. Diagram of Section of Stick and Handler Vats for Vegetable Tanning Calfskins. Letters are permanent designations for the vats; the liquor numbers change after each cleaning period.

On the first working day of the new section, take 150 calfskins, after deliming and bating as described in Chapter 9, weigh them and record as bated weight. Tack them onto sticks and hang them head down into vat No. A-1. The number of sections operating simultaneously must be sufficient to take care of total production.

On the second working day:

- 1. Move pack No. 1 into vat No. B-2.
- 2. To vat No. A-1, add 6 gals. stock liquor per 100 lbs. bated weight of pack No. 1 and mix well.
- 3. Put new pack No. 2 into vat No. A-1, running overflow to vat No. F-0.

On the third working day:

- 1. Move pack No. 1 into vat No. C-3.
- To vat No. B-2, add 6 gals. stock liquor per 100 lbs. bated weight of pack No. 1 and mix well.
- 3. Move pack No. 2 into vat No. B-2, running overflow to vat No. F-0.
- To vat No. A-1, add 6 gals. stock liquor per 100 lbs. bated weight of pack No. 2 and mix well.
- 5. Put new pack No. 3 into vat No. A-1, running overflow to vat No. F-0.

On the fourth working day:

- 1. Move pack No. 1 into vat No. D-4.
- To vat No. C-3, add 6 gals. stock liquor per 100 lbs. bated weight of pack No. 1 and mix well.
- 3. Move pack No. 2 into vat No. C-3, running overflow to vat No. F-0.
- To vat No. B-2, add 6 gals. stock liquor per 100 lbs. bated weight of pack No. 2 and mix well.
- 5. Move pack No. 3 into vat No. B-2, running overflow to vat No. IF-0.
- To vat No. A-1, add 6 gals. stock liquor per 100 lbs. bated weight in pack No. 3 and mix well.
- 7. Put new pack No. 4 into vat No. A-1, running overflow to vat No. F-0.

On the fifth working day:

- 1. Move pack No. 1 into vat No. E-5.
- To vat No. D-4, add 5 gals. stock liquor per 100 lbs. bated weight of pack No. 1 and mix well.

- 3. Move pack No. 2 into vat No. D-4, running overflow to vat No. F-0.
- 4. To vat No. C-3, add 6 gals. stock liquor per 100 lbs. bated weight of pack No. 2 and mix well.
- 5. Move pack No. 3 into vat No. C-3, running overflow to vat No. F-0.
- To vat No. B-2, add 6 gals. stock liquor per 100 lbs. bated weight of pack No. 3 and mix well.
- 7. Move pack No. 4 into vat No. B-2, running overflow to vat No. F-0.
- 8. To vat No. A-1, add 6 gals. stock liquor per 100 lbs. bated weight of pack No. 4 and mix well.
- 9. Put new pack No. 5 into vat No. A-1, running overflow to vat No. F-0.

On the sixth working day:

- 1. Haul out pack No. 1, remove from sticks and pile the skins flat, one by one, into vat No. G-1.
- To vat No. E-5, add 5 gals. stock liquor per 100 lbs. bated weight of pack No. 1 and mix well.
- 3. Move pack No. 2 into vat No. E-5, running overflow to vat No. J-0.
- To vat No. D-4, add 5 gals. stock liquor per 100 lbs. bated weight of pack No. 2 and mix well.
- 5. Move pack No. 3 into vat No. D-4, running overflow to vat No. F-0.
- 6. To vat No. C-3, add 6 gals. stock liquor per 100 lbs. bated weight of pack No. 3 and mix well.
- 7. Move pack No. 4 into vat No. C-3, running overflow to vat No. F-0.
- 8. To vat No. B-2, add 6 gals. stock liquor per 100 lbs. bated weight of pack No. 4 and mix well.
- 9. Move pack No. 5 into vat No. B-2, running overflow to vat No. F-0.
- To vat No. A-1, add 6 gals. stock liquor per 100 lbs. bated weight of pack No. 5 and mix well.
- 11. Put new pack No. 6 into vat No. A-1, running overflow to vat No. F-0.

On the seventh working day:

- 1. Move pack No. 1 into vat No. H-2.
- To vat No. G-1, add 2½ gals. stock liquor per 100 lbs. bated weight of pack No. 1 and mix well.
- 3. After removing from sticks, move pack No. 2 into vat No. G-1, running over-flow into vat No. J-0.
- 4. To vat No. E-5, add 5 gals. stock liquor per 100 lbs. bated weight of pack No. 2 and mix well.
- 5. Move pack No. 3 into vat No. E-5, running overflow to vat No. J-0.
- To vat No. D-4, add 5 gals. stock liquor per 100 lbs. bated weight of pack No. 3 and mix well.
- 7. Move pack No. 4 into vat No. D-4, running overflow to vat No. F-0.
- 8. To vat No. C-3, add 6 gals. stock liquor per 100 lbs. bated weight of pack No. 4 and mix well.
- 9. Move pack No. 5 into vat No. C-3, running overflow to vat No. F-0.
- To vat No. B-2, add 6 gals. stock liquor per 100 lbs. of bated weight of pack No. 5 and mix well.
- 11. Move pack No. 6 into vat No. B-2, running overflow to vat No. F-0.
- 12. To vat No. A-1, add 6 gals. stock liquor per 100 lbs. bated weight of pack No. 6 and mix well.
- 13. Put new pack No. 7 into vat No. A-1, running overflow to vat No. F-0.

On the eighth working day:

- 1. Move pack No. 1 into vat No. I-3.
- To vat No. H-2, add 2½ gals. stock liquor per 100 lbs. bated weight of pack No. 1 and mix well.
- 3. Move pack No. 2 into vat No. H-2, running overflow to vat No. J-0.
- 4. To vat No. G-1, add 2½ gals. stock liquor per 100 lbs. bated weight of pack No. 2 and mix well.
- 5. After removing from sticks, move pack No. 3 into vat No. G-1, running over-flow into vat No. I-0.
- To vat No. E-5, add 5 gals. stock liquor per 100 lbs. bated weight of pack No. 3 and mix well.
- 7. Move pack No. 4 into vat No. E-5, running overflow to vat No. J-0.
- 8. To vat No. D-4, add 5 gals. stock liquor per 100 lbs. bated weight of pack No. 4 and mix well.
- 9. Move pack No. 5 into vat No. D-4, running overflow to vat No. F-0.
- To vat No. C-3, add 6 gals. stock liquor per 100 lbs. bated weight of pack No. 5 and mix well.
- 11. Move pack No. 6 into vat No. C-3, running overflow to vat No. IF-0.
- 12. To vat No. B-2, add 6 gals. stock liquor per 100 lbs. bated weight of pack No. 6 and mix well.
- 13. Move pack No. 7 into vat No. B-2, running overflow to vat No. F-0.
- 14. To vat No. A-1, add 6 gals. stock liquor per 100 lbs. bated weight of pack No. 7 and mix well.
- 15. Put new pack No. 8 into vat No. A-1, running overflow to vat No. F-0.

On the ninth working day:

- 1. Haul out pack No. 1 and pile flat on truck.
- To vat No. I-3, add 2½ gals. stock liquor per 100 lbs. bated weight of pack No. 1 and mix well.
- 3. Move pack No. 2 into vat No. I-3, running overflow to vat No. J-0.
- 4. To vat No. H-2, add 2½ gals, stock liquor per 100 lbs, bated weight of pack No. 2 and mix well.
- 5. Move pack No. 3 into vat No. H-2, running overflow to vat No. J-0.
- To vat No. G-1, add 2½ gals. stock liquor per 100 lbs. bated weight of pack No. 3 and mix well.
- 7. After removing from sticks, move pack No. 4 into vat No. G-1, running over-flow into vat No. I-0.
- 8. To vat No. E-5, add 5 gals. stock liquor per 100 lbs. bated weight of pack No. 4 and mix well.
- 9. Move pack No. 5 into vat No. E-5, running overflow to vat No. I-0.
- To vat No. D-4, add 5 gals. stock liquor per 100 lbs. bated weight of pack No. 5 and mix well.
- 11. Move pack No. 6 into vat No. D-4, running overflow to vat No. F-0.
- 12. To vat No. C-3, add 6 gals. stock liquor per 100 lbs. bated weight of pack No. 6 and mix well.
- 13. Move pack No. 7 into vat No. C-3, running overflow to vat No. F-0.
- 14. To vat No. B-2, add 6 gals. stock liquor per 100 lbs. bated weight of pack No. 7 and mix well.
- 15. Move pack No. 8 into vat No. B-2, running overflow to vat No. F-0.
- 16. To vat No. A-1, add 6 gals. stock liquor per 100 lbs. bated weight of pack No. 8 and mix wen.
- 17. Put new pack No. 9 into vat No. A-1, running overflow to vat No. F-0.

The foregoing procedure has carried the first pack of skins entirely through the section and the indefinite continuation of the system is obvious from the description. It is possible to move the skins from one stick vat to another by hand, taking them one or two at a time. In this case, the supporting frames are left in the vat. Mr. Albert F. Gallun, Jr. developed a system for moving them mechanically that is much more economical and time saving. It is shown in operation in Fig. 172.

The two supporting frames in each stick vat are joined together by means of heavy cross beams. An electrically driven hoist operates from overhead rails so that it can be placed directly over any vat in the yard. It is equipped to raise both frames of any stick vat with all the skins suspended from their sticks and to move the whole pack to any other vat in the yard. For a new pack from the bate, the frames are placed on a support above the floor level and each skin is hung into



Courtesy A. F. Gallun & Sons Corp.

Fig. 172. Mechanical Device for Moving Calfskins in Vegetable-tan Yard.

its frame after being tacked onto a stick. The whole pack can then be examined for folds and pleats before being immersed in the first stick liquor. When coming from the fifth stick vat, the frames are again placed on supports above the floor level and the skins are removed by hand, one by one; the tacks are withdrawn and the skins are thrown, one by one, into the first handler vat, care being taken to have them all lie out flat in a horizontal position to avoid creasing. Movement from one handler vat to another is by hand to insure against any creasing.

Each stick vat has a total capacity of about 4500 gals. If the average weight of a pack of skins is 1500 lbs., the overflow stick vat will receive as a daily average 90 gals. each from stick vats No. 1, No. 2 and No. 3 and 75 gals. from stick vat No. 4, a total of 345 gals. per day, which will cause it to be filled to the point of three-quarters of its capacity in about 10 days. Each handler vat has a capacity of about 1125 gals. With the same average weight per pack, the overflow handler vat will receive daily 75 gals. from stick vat No. 5 and 37½ gals. each from the 3 handler vats, a total of 187½ gals. daily, which would cause it to be filled in only about 6 days. Actually, this discrepancy in filling time is not allowed to happen. The overflow from the fifth stick vat is run either to the overflow stick vat or to the overflow handler vat in such proportion that the overflow stick vat is filled to three-quarters of its capacity when the overflow handler vat is just filled.

When this occurs, the overflow handler vat becomes the third handler vat and

receives the pack coming from the second handler vat. When the pack is removed from the former third handler vat, it becomes the second handler vat and receives the pack from the first handler vat. The former second handler vat becomes the first handler vat and receives the stock from the fifth stick vat. The liquor from the former first handler vat is pumped into the overflow stick vat to complete the filling of it. The emptied former first handler vat then becomes the new overflow handler vat.

The former overflow stick vat now becomes the fifth stick vat, and receives the stock from the fourth stick vat. The former fifth stick vat now becomes the fourth and receives the stock from the third stick vat. Similarly, the former fourth becomes the new third, the former third becomes the new second and the former second becomes the new first stick vat. After the stock is removed from the former first stick vat, its liquor is run to the sewer, it is cleaned, if necessary, and becomes the new overflow stick vat. The whole change-over takes place within the day and is really quite simple.

This change-over is made every time the overflow stick vat becomes filled to the three-quarter mark with liquor and the first stick liquor is run to the sewer. There is one more procedure to be observed that was designed to save tannin. The first stick liquor usually contains about 0.5 percent tannin, as determined by the official method, and this represents a substantial money value in a large tannery. The foreman of the yard can tell several days in advance when the change-over is to take place. For the two days before the change, no stock liquor is added to the first stick vat, but the amount of stock liquor that would have been given to it is added to the other stick vats, being divided equally between them. The liquor run to the sewer is then practically exhausted of its tannin. There may be times when it is deemed inadvisable to allow a pack of bated calfskins to remain in an exhausted liquor over night. By providing an extra stick vat to the system, it can be arranged to leave the fresh pack in the weak liquor for only an hour or two before moving it into the second stick vat.

Temperature plays an important part in tanning. It is desirable to keep the temperature of the liquors as nearly constant as possible at some point between 70 and 80° F.

If the deliming of the stock is not done efficiently, there will be a danger of the pH values of the liquors rising so high as to cause trouble, and control may become necessary by occasional additions of acid to the liquors. The pH value of the first stick liquor should never be allowed to rise above 5.0. Whenever it does, dilute sulfuric acid should be added during the strengthening of the liquor to bring the pH value between 4.7 and 5.0.

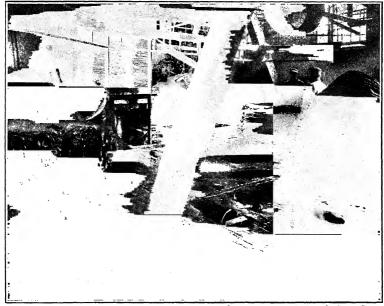
Variations in thickness of the skins may be responsible for upsetting the tannin strengths of the liquors, and so it is desirable to make occasional analyses of the liquors and adjust them by increasing or decreasing the amounts of stock liquor used in strengthening.

After the section is in full operation, the tannin strengths and pH values that it is desirable to maintain are as follows:

Vat	% tannin	pH value
1st stick	0.5	5.0
2nd stick	0.8	4.7
3rd stick	1.1	4.4
4th stick	14	4.1
5th stick	1.6	3.9
1st handler	1.8	3.7
2nd handler	2.0	3.6
3rd handler	2.2	3.5

When necessary to control pH value, this can usually be done by adding sulfuric acid to the first stick liquor when strengthening, to bring its pH value down to a point between 4.7 and 5.0. When necessary to control tannin strengths, one merely has to vary the volume of stock liquor per unit of bated weight used in strengthening. The initial barkometer readings will range from about 3 to 14, but they will rise with use for the same tannin content according to the amounts of lime and other foreign materials brought into the section by the bated skins, and also according to the increase in ratio of non-tannins to tannin, which always occurs during tanning. The barkometer range may increase with time from 3 to 14 to 12 to 18.

After the first cleaning period, the order of the vats in the section will be as follows: A-0, B-1, C-2, D-3, E-4 and F-5 for the stick vats, and G-0, H-1, 1-2 and J-3. The bated stock will go directly into B-1, then into C-2, etc., and the overflow vat will be A-0. Once a section is established, it will be found extremely simple to maintain it, especially if assisted by occasional analyses.



Courtesy A. F. Gallun & Sons Corp.

Fig. 173. Hydraulic Pressing of Vegetable-tanned Calfskins to Remove Water Preparatory to Splitting and Shaving.

The stock taken from the handler vats is not fully tanned, but is to be returned for retaining after splitting and shaving, all of which will be described in Chapter 14. After the pack is taken from the last handler vat, put it into a drum and rinse it by washing in running water for one minute, and then pile it back on a flat truck.

At this stage, the stock contains about 75 percent by weight of water, which is too much for proper handling in splitting and shaving. It must be reduced to about 50 percent. This means that the stock must be freed from about two-thirds of its

total water content. This is best done by pressing the water out of it. The skins are folded singly into neat squares and piled in a hydraulic press. The pressure is then applied and continued until water no longer exudes from the pile. This may require several hours, but the stock may safely be left in the press over night. In Fig. 173 a pile of vegetable-tanned calfskins may be seen in the hydraulic press in the left background. To the left of the press, a workman may be seen folding and piling skins for the next pressing.

The liquor pressed from a pack of 1500 lbs. of stock amounts to about 90 gals. of good handler liquor. The press is equipped with a tank into which the liquor pressed from the stock is drained. It is finally emptied into overflow handler vats and represents a considerable saving in tannin.

After pressing, the skins are tightly packed and creased and must be opened up to be handled properly in splitting and shaving. This is done by putting them into a dry drum revolving at about 15 revolutions per minute. When the stock is opened up properly, it is removed from the drum and sent to the splitting room.

Vegetable Tanning Pickled Calfskins

One of the many advantages of pickling as described in Chapter 9 is that it will remove or greatly minimize salt stains. Pickled skins can be vegetable-tanned in much the same manner as bated skins, but certain precautions must be taken or the stock will be ruined. Salt is used in pickling to prevent inordinate acid-swelling and gelatinization of the stock. If a pickled calfskin were suspended in the first stick liquor described above, the salt would diffuse out of it and into the liquor, but the salt concentration of the liquor would be too low to prevent acid-swelling and gelatinization of the skin. It would be completely ruined in a few hours.

Pickled stock can be vegetable-tanned safely only when the tan liquors contain enough salt to prevent the destructive acid-swelling until the stock is tanned to the point that it no longer swells in acid solution. In making up the *stock liquor*, it is important to avoid tanning materials that are precipitated by acid and salt. Cutch and wattle are the two extracts most resistant to precipitation by acid and salt, but quebracho is readily precipitated and should not be used for the stick or handler liquors. The stock liquor for pickled stock may be made up exactly like that for bated stock, except for the substitution of wattle for quebracho on a tannin basis.

Separate yards should be used for tanning bated and pickled stock, and their liquors should never be intermixed. The procedure given above for bated stock can be used for pickled stock with the following changes: The stock liquor is made by dissolving 400 lbs. of solid cutch extract, 400 lbs. of solid wattle extract and 1000 lbs. of liquid spruce extract in water and diluting to 1500 gals. with water. In starting a section for the first time, follow the rule for bated stock in making up both stick and handler liquors, but to vat No. A-1 add 1125 lbs. of salt, to vat No. B-2 900 lbs., to vat No. C-3 650 lbs., to vat No. D-4 560 lbs., to vat No. E-5 450 lbs., to vat No. G-1 75 lbs., to vat No. H-2 50 lbs. and to vat No. I-3 25 lbs. Add the salt after the stock liquor in each vat has been diluted with water. but before making up to final volume. Mix well until all the salt has dissolved and then make up to final volume. Mix well again, and the liquors are ready for use. Add no more salt until after the first cleaning of the section. With each forward movement of the stock, add stock liquor per 100 lbs. of pickled weight in the same amount as required per 100 lbs. of bated weight for the bated stock. After the first stick liquor in vat No. A-1 has been run to the sewer and vat No. B-2 becomes the new first stick as vat No. B-1, before putting fresh pickled stock into it, take the

barkometer reading; if it is below 40°, add enough salt to raise it to 40°. Then put the new stock into it. In the same manner, take the barkometer reading of each vat in the section and add salt enough to bring the barkometer readings to those shown below:

Vat	° barkometer	% tannin	pH val
1st stick	40	0.5	2.7
2nd stick	32	8.0	3.0
3rd stick	28	1.1	3.2
4th stick	26	1.4	3.3
5th stick	26	1.6	3.3
1st handler	26	1.8	3.3
2nd handler	26	2.0	3.3
3rd handler	26	2.2	3.3

If the barkometer reading is above the value indicated, add no more salt. The pH values indicated are merely to serve as a guide, no pH control being necessary. The liquors should be analyzed for tannin occasionally and adjustments made in the amounts of stock liquor added per 100 lbs. of pickled weight. In weighing the stock for either bated weight or pickled weight, it should be allowed to drain under fixed conditions for a fixed length of time. In either the bated or the pickled condition, nearly 80 percent of the weight of stock represents water. The longer a pack is allowed to drain, the less it weighs, even though the total weight of leather-making protein does not change. Light skins will contain more water than heavier ones. Usually pickled stock will weigh less than bated stock for the same protein content. For efficient operation, the conditions immediately preceding the weighing of the stock should be fixed as rigidly as possible, and then the amounts of stock liquor to add to the vats in strengthening should be determined by comparing the occasional analyses with the tannin values for the different vats indicated above.

Except for the differences indicated, the procedures for pickled stock are exactly like those for bated stock. For either type of stock, the plumpness and thickness of the final leather can be controlled by varying the proportion of cutch to wattle in the stock liquor for pickled stock, and of cutch to quebracho in the stock liquor for bated stock. As was pointed out in Chapter 10, cutch has a high fixation value, and both wattle and quebracho have low fixation values. When the demand for heavier types of calf leather is great, the thickness and weight can be increased by increasing the proportion of cutch. When lighter weights are in demand, it is not desirable to reduce the thickness by splitting, because this greatly lowers the strength and durability of the leather. Thinner leather of desirable strength can be obtained by increasing the proportion of wattle or of quebracho in the stock liquors. A cross-section of vegetable-tanned calf leather is shown in Fig. 174.

Calfskins can be vegetable-tanned in a drum in less than one day by giving them a pretannage with Calgon, but this will be described in Chapter 13.

Vegetable Tanning Sheepskins

Most sheepskins arrive at the tannery in the pickled condition, having previously been dewooled and bated. Sheepskins contain a large and very variable amount of natural grease which it is desirable to remove before tanning. There are many and varied methods of degreasing sheepskins, but one method will illustrate the principle involved. Tanners should be cautioned never to wash pickled stock with water alone, because just as soon as the salt is washed out of the skins, acid-swelling begins and the stock is destroyed by gelatinization. Being loose in structure, sheepskins are liable to damage from too severe mechanical

action. In drumming sheepskins, it is desirable to keep the speed below about 12 revolutions per minute. One method of degreasing follows:

Put a pack of 1000 lbs. of pickled sheepskins into a drum, start the drum running and add 200 lbs. of salt dissolved in 250 gals. of water at 100° F. Run 10 minutes and add first 10 gals. of kerosene and then 2 gals. of sulfonated cod oil



Fig. 174. Vertical Section of Vegetable-tanned Calf Leather.

Location: butt.

Thickness of section: 40 microns, or 0.00158 inch.

Magnification: 75 diameters.

and run 1 hour. Then drain the stock, pile on a hydraulic press, and press until no more liquor drains off. Then put the pack back into the drum, start the drum running and add 200 lbs. of salt dissolved in 250 gals. of water at 90° F. Run 30 min.; then dump the pack, pile flat on a truck, and send to be tanned. There are many commercial preparations on the market for degreasing, and some tanners eliminate the pressing operation. Some accumulate the degreasing solutions and recover the extracted greases, kerosene and the salt liquors for reuse.



Fig. 175. Vertical Section of Vegetable-tanned Sheep Leather.

Location: butt.
Thickness of section: 30 microns, or 0 00118 inch.
Magnification: 46 diameters.

Dissolve 325 lbs. of gambier extract, 120 lbs. of solid wattle extract and 50 lbs. of Leukanol (a synthetic tannin to be described in Chapter 13) in water to make a total volume of 250 gals. at 75° F. Put the pack of 1000 lbs. pickled weight of sheepskins into the drum, start it running and add 75 lbs. of salt in 125 gals. of water at 75° F. Run 5 min. and add 50 gals. of the above tan liquor. After running the drum for 10 min. longer, add another 50 gals.; 20 min. later, add another 50 gals.; 20 min. later, add the remaining 100 gals. and continue to run the drum until the time after the first addition of tan liquor is three hours. Then dump the pack, pile the skins on wooden horses and let stand over night. Next day, flesh the stock and put it back into the tanning drum and repeat exactly the tanning procedure of the day before. After dumping the pack, pile the skins on wooden horses, let stand over night again, reflesh and send to be colored and fatliquored. A cross-section of vegetable-tanned sheepskin, taken before finishing, is shown in Fig. 175.

The possible variations of this procedure are almost limitless. Many different kinds of tanning materials may be used and each has its own effect upon the properties of the final leather. Some tanners prefer to tan only in a single liquor, but the cuttings must be made to insure that the tannins have completely penetrated through all parts of the skins. When it is desired to make very plump leather, cutch extract may be used to advantage.

Vegetable Tanning Hogskins

Hogskins can be vegetable-tanned by either of the methods described for calfskins by extending the time of tanning, if necessary, to insure complete penetration of the tannin. They can also be tanned by the method to be described later for sole leather. A very good method for most types of hogskins is to take skins that have been unhaired, bated and pickled by methods described in the earlier chapters and tan them in a drum. In order to avoid too violent action, it is best to have a drum about 7 feet in diameter and 7 feet wide, running at only 12 revolutions per minute. Although hogskins consist only of thermostat layer after unhairing and fleshing, they have a very dense structure into which the tannins may penetrate very slowly, if not assisted by mechanical action. Different skins vary so much in thickness and in the ease with which the tannins may penetrate that the time required for complete penetration may vary greatly. Moreover, the penetration may not be uniform; a cutting made during tanning may show complete penetration except for many isolated spots of raw skin throughout a skin. The skins should never be taken from the final tanning liquor until no raw spots show on any cutting. The skins naturally have a very coarse grain and its accentuation by drumming is much liked when the leather is to be used for saddles or for wallets.

Put a pack of 1000 lbs. pickled weight of stock into the tanning drum, start it running, and add a mixture of 50 lbs. of Leukanol and 100 lbs. of salt in 120 gals. of water at 70° F. and run for 30 minutes. Dilute 300 lbs. of solid wattle extract with water to make 150 gals. at 70° F. Add 50 gals. of this liquor and run for 1 hour. Then add 50 gals. more and run for another hour. Then add the remaining 50 gals. and run for 2 hours longer. Allow the stock to remain in the drum over night, but have the drum run for 1 minute out of each hour during the night to guard against uneven coloring. Next morning haul out the stock, press it in a hydraulic press, wheel it to open up the skins and then split or shave it as may be required.

Have on hand a stock liquor of bisulfited quebracho extract containing 4 percent of tannin. Put the stock back into the drum and cover with this liquor. Run until the skins are completely struck through in all parts, but for not less than 2 hours. Haul out the stock, pile it on trucks and let it stand over night. Then wash in

running water in a drum at 80° F. for 1 hour, pile and send to be fatliquored. The liquor drained from the drum is put back into storage and strengthened to 4 percent tannin for reuse.

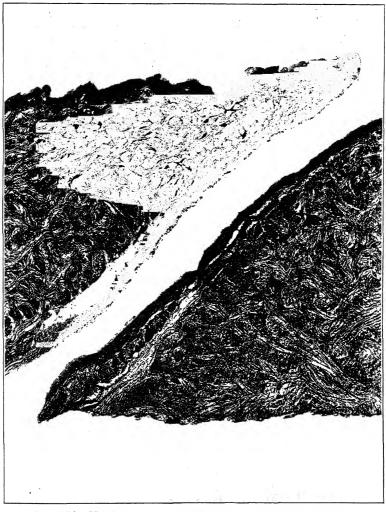


Fig. 176. Vertical Section of Vegetable-tanned Hog Leather.

Location: butt.

Thickness of section: 30 microns, or 0.00118 inch. Magnification: 46 diameters.

Fig. 176 shows a cross-section of hogskin taken after vegetable-tanning, but before finishing. It looks as though it were separated into two pieces, but this is merely the effect of cutting the section in a plane containing the hair follicle. By referring back to Fig. 24 of Chapter 1, it will be recalled that only a part of

the thermostat layer has a structure capable of conversion into leather, the remaining portion of the thermostat layer and all the reticular layer being made up of fatty tissues. The hair follicles thus pass completely through the leather.

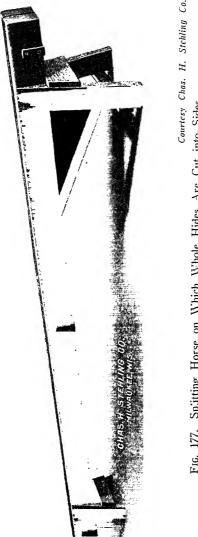


Fig. 177. Splitting Horse on Which Whole Hides Are Cut into Sides

Vegetable Tanning Sole Leather

Vastly more vegetable-tanned sole leather is produced than all other vegetabletanned leathers combined. The ten yards are divided into rocker vats and layaway vats, or layers. The rocker vats correspond to the stick vats used in making calf leather and the layers to the handler vats. In making sole leather, however, the vats are of necessity much larger and there are many more of them.

Rocker Yard

A typical rocker yard is made up of 10 sections of 20 vats each, or a total of 200 vats. Each section is independent of the others. When a pack of hides is put into a vat, it remains there until ready to be removed from the section; only the liquor moves. Each vat is 9 feet long by 8 feet wide and 5 feet deep, measured from the overflow outlet, having a capacity of about 2700 gals. Each vat is equipped with a wooden frame for supporting the stock; it is 7 ft., 10 in. long by 7 ft., 5 in. wide. At the midpoints of the length, on both sides, there are pivot pins which rest in the sockets in the sides of the vat, permitting the frame to rock, like a seesaw. The ends of the frame are either studded with pins, when sides are being tanned, or with grooves for holding the ends of poles, when whole hides are being tanned. To one end of each frame is attached a wooden shaft whose other end is operated by a rotating cam, which causes the frame to rock at the rate of 10 cycles per minute. The frame is rocked continuously.

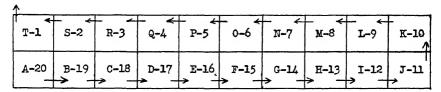


Fig. 178. Showing Arrangement of Vats in a 20-Rocker Section. Letters represent permanent designations of vats and numbers the order of increasing strength of liquors, which move in directions indicated by arrows.

When the stock is tanned as sides, it is customary to split the hides into sides either just before or after unhairing. This is done by placing the hide over a splitting horse like that shown in Fig. 177. The hide is placed over the horse so that its backbone line is directly over the groove running the length of the horse. With a sharp knife, a workman cuts the hide into two sides along the line of the backbone, using the groove as a guide. At the same time two holes are punched in each side 7 feet apart and about one-half inch from the backbone edge.

When the sides are hung into the liquor, leather straps with copper hooks at one end are used, having an overall length of 5 inches. A workman at each end takes a side, puts the hook through the hole in the side and then slips the loop of the leather strap over a pin in the end of the frame.

When whole hides are being tanned, each hide is hung over a pole, along the line of the backbone, and the pole is placed with its ends set in grooves at the ends of the frames. The sides or hides are hung on the frame in a row with the directions, head to tail, alternating. When whole hides are being tanned over poles, sometimes double poles are used, one being suspended from the other. Then a hide is hung over the lower pole and a second hide over the upper pole and flanking both sides of the lower pole. In this way, nearly twice as many hides can be hung in a vat. The general arrangement of a rocker section is shown in Fig. 178. The following description is for a section receiving daily 58 whole hides or 116 sides weighing 3480 lbs. after deliming and bating.

The letters are permanent designations of the vats and do not change. The

numbers are temporary designations of the liquors and change each working day. No. 20 is the strongest liquor. It is called *head-rocker liquor*. No. 1 is the most nearly exhausted liquor. It is called the *tail-rocker liquor*. The head-rocker liquor is made up each working day by taking all of the previous head-rocker liquor and adding to it waste liquor from the layers and enough fresh extract-liquor to make a liquor of 6 percent tannin.

The arrows show the direction of movement of the liquor through the section on one particular day. Between vat A and vat B, there is a pump log with an opening leading from the bottom of vat A to the top of vat B. A similar pump log is placed between each successive pair of vats in the direction of the arrows, each leading from the bottom of one vat to the top of the next vat in the series. There is also a pump log leading from the bottom of vat T to the top of vat A, completing the cycle. Each vat is also equipped with a bottom outlet and also an outlet at the normal liquor level to the sewer. All outlets can be closed. In the setup as shown in Fig. 178, the outlet from vat T to vat A is closed and the top outlet from vat T to the sewer is open.

The liquor in vat A-20 has a tannin strength of 6 percent and a pH value of 3.50. The liquor in vat T-1 has a tannin strength of 0.3 percent and a pH value of 5.00; it has passed over 20 lots of hides and has become practically exhausted. On the next working day, the hides are taken out of vat A-20 and its liquor is pumped to a mixing tank where it receives its proportionate share of waste liquor from the layers and enough fresh extract liquor to increase its volume by one-half and to give it a tannin content of 6 percent. The emptied vat A becomes the new tail rocker, A-1. The outlet from vat T to the sewer is closed and the outlet from the bottom of vat T to the top of vat A is opened. The outlet from the bottom of vat A to the top of vat B is closed. The overflow outlet from vat A to the sewer is opened. Then the new liquor is run onto vat B, causing a flow of liquors from vat B through C, D, E, etc. around to vat A, which becomes the new tail. After vat A becomes filled, waste liquor will overflow to the sewer in amount equal that of the increase in volume added to that used to run onto vat B. The new order of increasing strength of liquors in the section is now as follows: A-1, T-2, S-3, R-4, Q-5, P-6, O-7, N-8, M-9, L-10, K-11, J-12, I-13, H-14, G-15, F-16, E-17, D-18, C-19 and B-20. The fresh pack of hides from the bate is hung into vat A-1.

On the next working day, the stock in vat B-20 is hauled out and its liquor is pumped to the mixing tank where it receives the daily waste liquor from the layers and enough fresh extract to increase its volume by one-half and to give it a tannin content of 6 percent. The emptied vat B becomes the new tail rocker, B-1. The outlet from vat A to the sewer is closed and the outlet from the bottom of vat A to the top of vat B is opened. The outlet from the bottom of vat B to the top of vat C is closed. The overflow outlet from vat B to the sewer is opened. Then the new liquor is run onto vat C, causing a flow of liquors from vat C through D, E, F, etc. around to vat B, which becomes the new tail. After vat B becomes filled, waste liquor will overflow to the sewer in amount equal to that of the increase in volume to that used to run onto vat C. The new order of increasing strength of liquors in the section is now as follows: B-1, A-2, T-3, S-4, R-5, Q-6, P-7, O-8, N-9, M-10, L-11, K-12, J-13, I-14, H-15, G-16, F-17, E-18, D-19 and C-20. The fresh pack of hides from the bate is hung into vat B-1.

By a simple, daily repetition of this procedure, it will be seen that each working day, a pack of hides is withdrawn from the 20th liquor. This liquor is then pumped to the mixing tank and increased in volume by one-half by adding waste liquor from the layers and fresh extract to make a new liquor of 6 percent tannin, which is run onto what was the 19th liquor. The liquors then press over from one

vat to another until what was the head-rocker vat becomes filled with the most exhausted liquor and receives the fresh pack of hides from the bate. A fresh pack of hides hung into a tail liquor remains in the same vat for 20 working days, receiving the next stronger liquor each day until it is ready to be withdrawn from the vat. Each working day one-half of a vat of tail liquor is run to the sewer.

The liquor of 6 percent tannin which is run onto the new head rocker each working day is gradually *pressed* down through the system until finally wasted in the overflow from the tail liquor to the sewer. By the time it becomes a tail liquor, its tannin content has dropped to about 0.3 percent. The tannin percentages given are those found by the official method, which is still in use in most tanneries. This method always gives results that are too high; actually, a waste tan liquor showing 0.3 percent tannin by the official method contains less than 0.1 percent of true tannin, and so the waste is practically negligible.

If the total number of hides hung into each vat is the same, but their weight varies, the tannin requirements will vary because they are determined by the weight of the hides. It is desirable to record the bated weight of each pack entering a section, and to base the amount of tannin extract to add to the new head rocker upon the weight of each new pack entering the section. This can best be determined by experience in each individual tannery, but a satisfactory start can be made simply by following the rule of having the head liquor contain 6 percent of tannin.

After the average amount of tannin per 100 lbs. bated weight to be added to the head rocker has been determined, frequent analyses of the tail liquors should be made. If the amount of tannin found drops below 0.3 percent, the addition of tannin should be increased; if it rises above 0.3 percent, it should be decreased. A partial control is also possible by regulating the daily volume of overflow tail liquor to the sewer, which can be done by regulating the increased volume added to the head liquor in strengthening.

If the tanning extract mixture contains equal parts on tannin basis of cutch, chestnut and bisulfited quebracho extracts, a control over rate of penetration of tannin into the stock and of plumpness and yield of leather is made possible by varying the proportion of cutch to quebracho. By increasing the proportion of quebracho, the speed of penetration is increased, but the plumpness and yield are decreased. Conversely, increasing the proportion of cutch decreases the rate of penetration, but increases the plumpness and yield.

Upon coming from the head rocker, the hides are piled flat and allowed to remain over night. They are then sent to the layer vats for further tanning. At this point, the hides will generally be completely penetrated by tannin, but the increased tanning time results in a further fixation of tannin by the hide protein, which results in plumper and firmer leather, which is desired for sole leather.

Layer Yard

For the rocker yard just described, the layer yard is made up of 10 sections of 21 vats each, or a total of 210 vats. These vats are of the same size and shape as the rocker vats. A typical section is shown in Fig. 179. A layer section is really made up of 7 smaller sections of 3 vats each. Each smaller section is designated by a letter and each vat in it by a number. The liquors in all 21 vats are made up before receiving a new pack of leather to contain 6 percent tannin. A pack from the rocker section is put into any one of the first layer vats (A-1 to G-1) and remains there for 7 working days. It is then moved over into the second layer vat of the same smaller section, where it remains for 7 more working days. It is then hauled out of the layer section.

Each layer or rocker vat has a total capacity of about 2700 gals., of which about 400 gals is occupied by hides and about 2300 gals by liquor. On a typical working day, the pack of hides in vat No. A-3 is hauled out of the section after having been for 7 working days in vat No. A-1, followed by 7 working days in vat No. A-2 and then 7 working days in vat No. A-3. Assuming that the pack has taken out enough tannin to reduce the strength of the remaining 2300 gals. of liquor in vat No. A-3

A-1	A-2	A-3
B-1	B-2	B - 3
C-1	C-2	C -3
D-1	D-2	D-3
E-1	E-2	E-3
F-1	F-2	F-3
G-1	G-2	G- 3

Fig. 179.

Showing Arrangement of Vats in a 21-Layer Section. Letters represent subsections and numbers order of movement of hides through subsection.

from 6 to 5 percent, run 300 gals. of used liquor from vat No. A-3 to the rocker mixing tank and then add 300 gals. of fresh extract liquor of 12 percent tannin, and mix well. Vat No. A-3 will now contain 2300 gals. of liquor of 6 percent tannin. Take the hides, one by one, from vat No. A-2 and throw them into vat No. A-3 so that they lie flat in a pile.

Assuming that the 2300 gals. of liquor left in vat No. A-2 has also had its tannin content reduced from 6 to 5 percent tannin, run 300 gals. to the rocker mixing tank and then add 300 gals. of fresh extract liquor of 12 percent tannin and mix well. Vat No. A-2 will now contain 2300 gals. of liquor of 6 percent tannin. Take the

hides, one by one, from vat No. A-1 and throw them into vat No. A-2 so that they lie flat in a pile.

Assuming that the 2300 gals. of liquor left in vat No. A-1 has also had its tannin content reduced from 6 to 5 percent tannin, run 300 gals. to the rocker mixing tank and then add 300 gals. of fresh extract liquor of 12 percent tannin and mix well. Vat No. A-1 will now contain 2300 gals. of liquor of 6 percent tannin. Take the pack of hides coming from the rocker section and throw them, one by one, into vat No. A-1 so that they lie flat in a pile.

On the next working day, haul the pack out of vat No. B-3 and repeat for subsection B exactly what was done with subsection A on the day before, putting the new pack from the rocker section into vat No. B-1. Each working day, the next subsection in order is handled in the same way through subsection G, after which subsection A is taken again, making the entire procedure continuous.

Each working day, the rocker mixing tank receives 900 gals. of waste layer liquor of 5 percent tannin and 2300 gals. of head-rocker liquor of about 5.8 percent tannin. To this is added about 142 gals. of fresh extract liquor of 12 percent tannin and about 108 gals. water to make a total of 3450 gals. of new head-rocker liquor of 6 percent tannin, which is added to the new head-rocker liquor, causing 1150 gals. of tail-rocker liquor to waste to the sewer.

After the pack is hauled out of the third layer, it is sufficiently well tanned to make good harness or strap leather, but in making sole leather, it is usually desired to do everything possible to increase the plumpness, solidity and yield of the leather and to incorporate into it properties particularly valuable in leather used for the soles of shoes. Since the subsequent operations are peculiar to sole leather, the description of them will be given in Chapter 18.

The procedure described above for the operation of the rocker and layer sections is relatively very simple when only well delimed and bated stock is tanned and when the tanning mixture consists of equal parts on tannin basis of bisulfited quebracho, cutch and chestnut extracts. Because the lime content of the bated stock is uniformly low and the natural pH value of the head rocker liquor is about 3.50, very little has to be done to control the pH value. In the routine operation of the yards, it will be found that the pH value of the tail liquor is about 5.0 and that it drops gradually to 3.5 as the head liquor is approached. If enough lime should be carried over to raise the pH value of the tail liquor above 5.0, acid should be added to it to keep it between 5.0 and 4.7. Although lactic acid is generally preferred for this, the writer has demonstrated that the much cheaper sulfuric acid can be used for this purpose with perfect satisfaction, since it is used only to neutralize a relatively small amount of lime in liquors nearly exhausted. The speed of the tanning increases rapidly with increase in temperature. It is important never to allow the temperature of the liquors to fall below 70° F. This can usually be taken care of by never allowing the temperature of the air in the yards to fall below 70° F.

If the average weight of a pack entering the rocker vats is greater than 3500 lbs. bated weight, more tannin will be required and this is easily provided by increasing the volume of liquor of 6 percent tannin put onto the new head-rocker liquor, allowing a corresponding increase in volume of exhausted tail liquor to run to the sewer. A good plan to start with is to put one gallon of liquor of 6 percent tannin onto the head rocker for each pound of bated weight of stock entering the tail rocker. Since approximately two-thirds of the liquor run onto the new head rocker came from the previous head rocker, it means only one-third gallon of new 6 percent liquor to be added to the section for each pound of bated weight

entering the section. Increasing the size of the packs must be done cautiously because crowding the vats may cause discolorations, low yields and flat leather. Merely increasing the amount of tannin added will not compensate for crowding.

Since the official method of tannin analysis is used almost universally in American tanneries, all percentages of tannin referred to in this chapter mean tannin as determined by the official method. In Table 28 of Chapter 10, values are given for the true tannin corresponding to tannin as determined by the official method for various pure extracts. A gallon of liquor of 6 percent tannin by the official method, when made from equal parts on tannin basis of quebracho, chestnut and cutch extracts, would contain 0.5 lb. tannin by official method, but only 0.35 lb. true tannin. Thus for each pound bated weight of stock entering a section, the section would receive about 0.113 pound of true tannin. The calculations for other tanning extracts can be made from the values given in Table 28. It should be remembered, however, that the values given in Table 28 are for the pure extracts only. With used liquors, the error in the determination of tannin by the official method is much greater than for pure extracts.

Once the system is established, the amount of 6 percent tan liquor added to the head rocker per unit of bated weight entering the tail rocker should be adjusted so that the tail liquor run to the sewer will contain 0.3 percent tannin by analysis. The rocker liquors also must ultimately be adjusted by analysis, although a start can be made simply by following the procedure as given.

Probably most sole-leather tanners do not use the simple mixture of tanning extracts described, but mixtures much more complex and containing also their own leachings of raw materials. In many sole-leather tanneries, the stock entering the tail rockers is still much plumped by lime and the rocker liquors must of necessity perform the function of deliming. In order to do this, they must contain sufficient quantities of acid, which is usually provided by adding sour liquors made from myrobalans or divi-divi to the head-rocker liquor. Often the raw materials are ground and extracted in the leach house to produce strong liquors; and these are allowed to ferment with the formation of large amounts of organic acids. In the case of well delimed stock, the optimum pH range of the liquors is from 5.00 in the tail rocker, dropping very gradually to 3.50 in the head rocker. For stock not delimed at all, the pH values must be much lower, and may range from 3.8 in the tail liquor to a point below 3.0 in the head rocker. For stock well delimed, such pH values result in destruction of the stock by acid swelling. In well delined stock, the acid penetrates into the hides much more rapidly than do the tannins, and causes inordinate swelling of the untanned interior portions of the hides.

In the case of stock still plumped by lime when in the rocker liquors, the acid is neutralized by lime just as soon as it starts to penetrate, and penetration by the tannin is speeded up by the alkaline condition of the stock. The result is that acid and tannin penetrate at almost the same rate, and the interior of the hides remains alkaline until the tannin reaches it and converts it into leather, which does not swell inordinately in contact with the acid liquors.

To one not intimately familiar with the routine operation of such a yard, this procedure is actually a very hazardous one; however, some tanneries have used it for many years and have gained a high reputation for producing unusually plump leather of high quality. Once a tanner has brought his whole system into a state of balance and determined the optimum pH values for his rocker liquors, he maintains these values by increasing or decreasing the proportion of acid tan liquor added to the head-rocker liquor based on his pH measurements, adding more when the pH value is high and less when it is low. The writer has examined hides that

had been in such liquors for more than a week and has found the untanned portions of the hide very strongly alkaline while the liquors in which the hides were hanging was very strongly acid. An interesting experience of a tanner operating such a yard illustrates one of its hazards. He became interested in trying to improve the grain of his leather by bating it properly and acquired the services of a man expert in bating. When this stock was put into the rockers, acid swelling set in and the stock was completely destroyed by acid swelling in a few days. The same kind of destruction would occur when pickled stock is being vegetable tanned, if liquors containing no salt were used. If the tanner who puts stock plumped with lime into his rocker liquors were to omit the addition of acid liquors, the rocker liquors would become alkaline and his leather would become badly discolored and of low quality and yield. Between the extremes of no deliming at all and complete deliming of the stock entering the rocker liquors, the yards must be operated on a correspondingly different basis of pH control of the individual liquors.

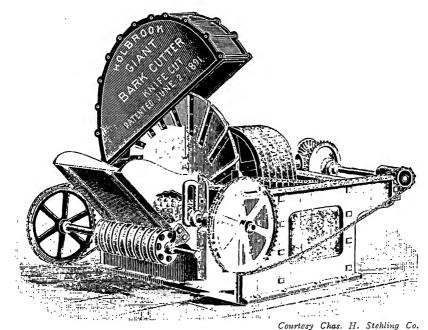


Fig. 180. Typical Tannery Bark Mill.

When hanging sides into rocker vats according to the procedure described above, it is desirable to have the vat completely filled with liquor both before they are hung in and while they are being taken out, to prevent bagging of the sides, which becomes permanent upon tanning. After all the sides are in place, it is a safeguard to pass a stick between each pair to separate them; otherwise the tannin may not immediately color areas that are in contact, and such areas may remain lighter in color than the area as a whole, even after the leather has been finished. Such areas are known as kiss spots. The frames are rocked continuously in order to keep liquor flowing over the areas to prevent touching and kiss spots. The rocking motion does not speed up the tanning measurably.

Some tanners have as few as 8 vats in a rocker section and use many more layer vats. In some tanneries, the layer sections are very elaborate and the stock may remain in the liquors for several months. Other tanners use no layers at all, but take the stock from the rocker vats, even before being completely penetrated by tannin, and complete the tanning in a drum.

The Leach House

In many sole leather tanneries, the *leach house* contains a very elaborate system of bark grinders, leaching tanks, mixing tanks, storage tanks and pumps. Fig. 180 shows a typical bark mill. The bark, or other raw material, is fed into it through a hopper and meets a series of sharp, rotating knives, which cut it up into pieces fine enough to be leached readily with hot water. Operating at a speed of 550 r. p. m. with 35 horsepower, it is capable of grinding 3 cords of bark per hour.

Practically all the tanks in the leach house are built of either cypress, fir, or California redwood. In leaching the ground raw material in a tank, it is placed on a false bottom, like that shown in Fig. 181. For proper leaching, it is essential

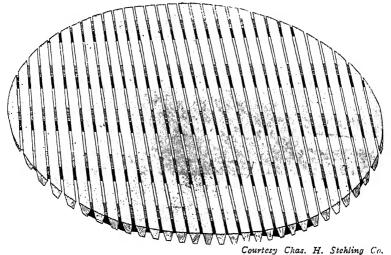
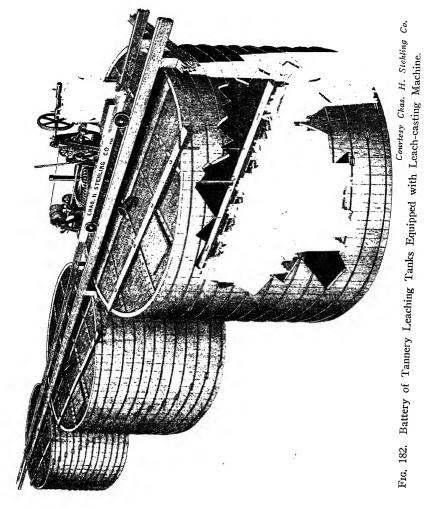


Fig. 181. Typical False Bottom Used in Tannery Leaching Tanks.

to have the ground material evenly distributed over the false bottom, and for that purpose also the leach-casting machine is used.

Fig. 182 shows a battery of leaching tanks with a leach-casting machine set on tracks running over the tops of the tanks, the machine being so equipped that it can readily be moved from one tank to another. The leach-casting machine is put in place whenever a tank is being filled with the raw, ground, tanning material. It is run while the material is being dumped onto the false bottom through an opening in the top of the tank and it distributes the material evenly over the false bottom. By having the tops of the tanks covered, the dust which contains much tannin is kept inside the tank. Fig. 183 shows the leach casting machine in greater detail. When the spent bark is to be removed, the machine sweeps it up and permits it to be removed while still hot, thus facilitating its drying before being put under the boilers as fuel.

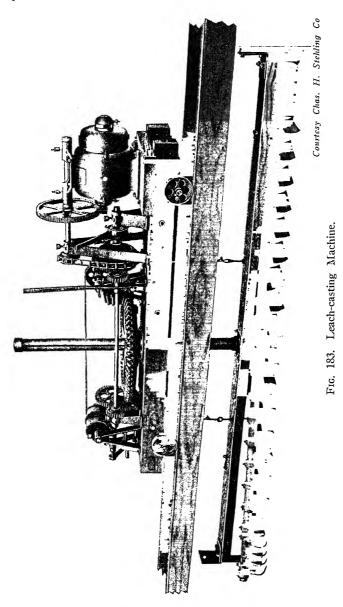
Fig. 184 shows the type of copper coil used in heating the liquors. It is equipped with inlet and outlet for steam. The copper tubing is usually from 1 to $1\frac{1}{2}$ inches in diameter and from 100 to 125 feet in length. It is placed below the false bottom.



The number and sizes of the tanks in a leach house is determined, of course, by the size and requirements of the tannery and by the number of different tanning materials used. Probably the largest tanks ordinarily used are 20 feet in diameter by 20 feet high, having a capacity of more than 50,000 gals each. From this extreme, there are all sizes down to several hundred gallons each.

In leaching raw materials, the number of tanks required depends upon the proportion of water to raw material used in each tank. When the proportion of water

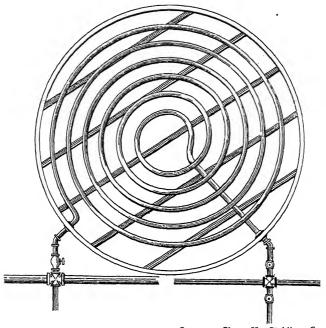
is greater, fewer tanks are required. Some tanners fill a tank to about one-quarter of its capacity with raw material and use a battery of 8 tanks. However, this depends upon the nature of the raw material and the ease with which its tannin is



extracted. The final determination of the number of tanks is made by analyzing the material after each extraction. When the tannin content reaches a point so low that further extraction is not economical, the spent raw material is discarded. The

number of extractions required to reach this point represents the number of tanks required for leaching.

When the number is 8, they are set up as a battery equipped with a pump for transferring the liquor from one tank to another. Since contact with iron must be avoided, the pump and all piping must be made of brass. A typical tan-liquor pump is shown in Fig. 185. In starting a battery, tank No. 1 is given its charge of ground raw material (about one-quarter of the volume of the tank). The false bottom is placed in the tank to a depth of about one-half. The raw material is placed on it. Below the false bottom is placed the heating coil and above it the rotary arms of the leach-casting machine, which keeps the raw material evenly distributed



Courtesy Chas. H. Stehling Co.

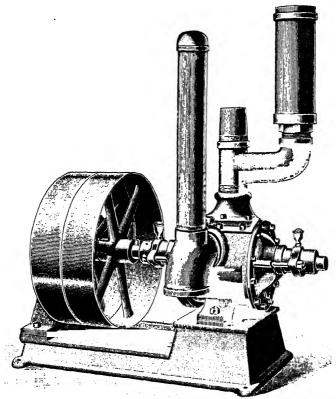
Fig. 184. Copper Heating Coil for Leaching Tanks.

over the false bottom and assists the extraction by mechanical agitation. The tank is filled with water at 180° F., and this temperature is maintained by the heating coil. Next day, tank No. 2 is given its charge of raw material and the liquor from tank No. 1 is pumped onto it. Then fresh water is run into tank No. 1 and then extraction is continued. On the next day, tank No. 3 is given its charge of raw material and the liquor from tank No. 2 is pumped onto it, the liquor from tank No. 1 is pumped into tank No. 2 and fresh water is run into tank No. 1. On each successive day, fresh raw material is put into the tank one higher in number than the last previous one receiving fresh raw material, and it receives the liquor from that last previous one. On the day after tank No. 8 has been charged with fresh raw material and received the liquor from tank No. 7, the liquor is run to the storage tank. Then the spent material in tank No. 1 is discarded after its liquor has been pumped to tank No. 2. Then tank No. 1 is

charged with fresh raw material and it receives the second liquor from tank No. 8. The cycle is thus continuous.

Each working day, the liquor that has passed over 8 charges of material is pumped to the storage tank and the spent material that has been extracted 8 times is discarded, its tank then being charged with fresh raw material.

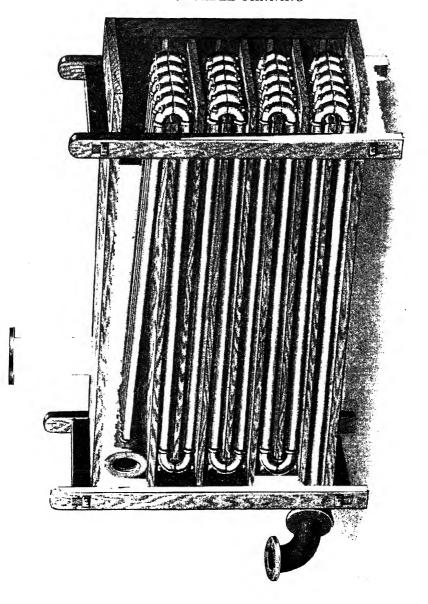
In order to minimize oxidation, it is desirable to cool the strong liquor before running it to the storage tank. This can be done by pumping the liquor first over brass coils containing running cold water set in a tank like that shown in Fig. 186 and then on to the storage tank. The same equipment can be used to heat yard liquors, in which case steam is turned into the copper coils.



Courtesy Chas. II. Stehling Co.

Fig. 185. Brass Rotary Belt Pump Used for Pumping Vegetable-tan Liquors.

If myrobalans, divi-divi or valonia is extracted to get acid liquors to control the pH values of the rocker liquors, fermentation is allowed to proceed in the storage tank, which can be followed by periodic determinations of pH value, which decreases with increasing formation of acid. Such liquors are used to regulate the pH values of the rocker liquors to the values found best for the conditions of the individual tannery. The amount of liquor added to the head-rocker vat is increased when it is desired to lower the pH values of the rocker liquors and decreased when it is desired to raise them.



When tanning extracts are being dissolved, it is necessary to use only a single tank equipped with a copper heating coil and with a stirring device consisting of long bladed arms rotating in a horizontal plane about a vertical shaft.

The bisulfiting of quebracho extract has already been described in Chapter 10. When cutch is used with quebracho in the yard liquors, it is desirable to mix both together and then to bisulfite the mixture exactly as for quebracho alone, using 5 lbs. of sodium bisulfite for each 100 lbs. of total solids in the mixture.

It is customary to have at least one large storage tank for each kind of tanning material. Liquors extracted directly from raw materials are not diluted for storage, but solid and liquid extracts are usually dissolved in water at 180° F. and then cooled and diluted to a gravity of about 25° Baumé for storing. Storage tanks are provided also for the mixtures to be used in the layer and rocker vats. It is also customary to have mixing tanks wherein head rocker liquors, layer liquors and extract liquors can be mixed quickly for running to the vats.

Dilutions are usually adjusted by gravity measurements made with hydrometers with the Baumé, Twaddell or barkometer scales, but the tannin content in relation to gravity should always be known by the tanner. Since the relation of tanning content to specific gravity is different for each tanning material and mixture and for used yard liquors, the tanner should secure these relations for his own set of conditions.

Some tanners use only prepared extracts for tanning; for them the control of the leach house is a very simple matter. But many tanners leach raw material to lower the cost of their tanning materials. They may be located close to the sources of certain raw material or they may find a market for the spent tanning material; it has been possible in some localities to sell the spent oak bark for more than the cost of the raw bark. When they want myrobalans or other raw material primarily for the production of acid, they usually find it cheaper to buy the raw materials. Sometimes they use raw materials in order to get certain color effects in the leather. However, raw barks sometimes become infected with mold growths that produce unnatural developments of acid, which may upset the balance of a tan yard.

Guarding Against Acid Swelling

If a raw hide is immersed in a pure solution of acid of pH value less than 5.0, it swells by absorbing water and becomes distorted because of the resistance to swelling of the elastin fibers in the grain layer. The vigor of this acid swelling increases at a rapid rate as the pH value is reduced from 5.0 to 2.4, the point of maximum swelling. Immediately after the swelling has taken place, if salt is added to the liquor in amounts greater than 4 oz. per gal., the swelling subsides. If a hide is allowed to remain in a highly swollen condition, it gradually gelatinizes and is destroyed.

During rainy weather, when bark is stored in open sheds, there is great danger of mold infection, and the bark may become coated with yellow incrustations of mold. These molds act upon the bark, producing considerable quantities of acids. Even the liquors obtained from the leaching of the bark continue to sour very rapidly when used in the vard liquors. Years ago, this type of acid fermentation ended in tragedy for a number of tanners to the writer's knowledge. To illustrate, in one case a tanner of harness leather was obtaining hemlock bark from a local source and leaching it himself to obtain his tanning liquors. He had operated in the same way for many years and had always produced a leather of high quality. One day he observed that the tannin was not penetrating with the usual speed into the Several days later, upon making cuttings of the leather, he noted that the raw middle layer did not have the usual whiteness of appearance, but was glassy and translucent. A week later, the middle layers of all the stock in the yard had become like jelly and the tanned grain and flesh layers could be pulled apart. The same thing happened to any fresh stock put into the yard. It was not long before every hide in the yard was completely ruined. In desperation, he emptied the yard and made up series of entirely new liquors, but again the stock put into them was ruined and so was the tanner, who went into bankruptcy.

This and other cases like it occurred before pH control became the rule in every tannery. However, the writer has been called in to save tanneries where this acid fermentation had gained a foothold, even though pH values were being measured daily. In the first tannery mentioned, it had been observed that a sour odor in the yards was very strong when the tragedy occurred; in the later cases, it had been observed that the pH values of the liquors had dropped from a range of 5.0 to 3.7 to a range of 4.5 to 3.0. An attempt had been made to neutralize the excess acid by adding soda ash to the liquors to raise the pH values to normal, but next day, the acid condition would be as bad as ever. The writer did the one obvious thing as an emergency measure in such cases, and that was to add to each liquor containing stock not yet fully penetrated by tannin 25 lbs. of salt to each 100 gals. In each case, all the stock was saved. This served as a temporary expedient until the moldy bark was disposed of, and once the liquors were again put in sweet condition, the use of salt was discontinued.

Some acid fermentation takes place in most liquors, but if the amount of acid formed is not greatly in excess of that required to neutralize the lime in the stock, no damage will be done.

These illustrations and all that they imply should be studied in greatest detail by all tanners who do not delime their stock but rely on acids formed by fermenting myrobalans to take care of the lime. They have an enormous advantage over the old tanner in pH control and systematic analyses, but they should remember that they are operating their liquors at pH values so low that destructive acid swelling of the stock would occur quickly, if it were not for the lime present in the stock. Although they might operate for many years without any trouble, they should resort to the use of salt when it does appear, but only as an emergency measure, to be discontinued after the trouble has been eliminated.

The writer believes that those tanners who properly delime and bate their stock and graduate the pH values of the rocker liquors from 5.0 in the tail to 3.5 in the head, without ever resorting to lower pH values to neutralize lime, have a better chance for survival.

Rapid Tanning of Sole Leather

Years ago, some tanners took more than a year to tan heavy steer hides for sole leather. With the advent of concentrated extracts and pH control, this time has been shortened to a few months. However, there are a few modern tanners who have reduced the tanning time considerably by replacing the rocker vats by tanning drums. If bated hides are drummed directly with tan liquor, they become so rough and broken up as to be unsalable. However, if they are first sufficiently penetrated by tannin in the rocker liquors, they may be given a mild drumming with safety. In one comparative test, the writer found that drumming stock with tan liquor for only 14 hours was equivalent to tanning it for 6 weeks in the layer vats.

For the drum tanning of sole leather, a drum 7 feet in diameter by 7 feet wide is used, which revolves at 12 revolutions per minute with a load of 1700 lbs. of wet leather. If the stock coming from the head rockers has not already been cut into sides, this is done and lots of 1700 lbs. each are made up. A lot is put into a drum and covered with 190 gals. of liquor of 12 percent tannin (made from equal parts on tannin basis of chestnut extract, bisulfited quebracho extract, and bisulfited cutch extract) at 70° F. The drum is run continuously for 12 hours, the stock is taken out and piled on a truck for 48 hours and the used liquor is run to a storage mixing tank. The stock on the truck is carefully covered to minimize oxidation and drying.

After being piled for 48 hours, the pack is put into a drum, covered with 500 gals. of water at 80° F. and run for one hour. It is then piled on a truck and the liquor is run to the storage mixing tanks. The liquors from both treatments run to this storage mixing tank are built up with fresh extract solutions to make a new stock liquor of 12 percent tannin. The stock on the truck is then moved on and treated exactly as though it had come from a layer section. The further treatments will be described in Chapter 18.

Vegetable Tanning Pickled Steer Hides

Although the writer has made some excellent sole leather from pickled steer hides, he knows of no tanner at the time of this writing that is pickling stock for tannage into sole leather. This is probably due to lack of familiarity with the procedure rather than any objection to it. Pickling calfskins for vegetabletanning is a well-established procedure and the value of the leather has been proved over many years to be fully as good as that tanned directly from bated stock. Pickling has the advantage of eliminating salt stains and other iron stains. It permits full and proper bating of the stock without danger of upsetting the balance of the tan yards. It does away entirely with the use of acid-forming materials, such as myrobalans, in the head-rocker mixture. When it is desired to run the beamhouse ahead of the tan yards, this can be done because the pickled stock can safely be kept at a temperature of 60° F. for at least two years. If desired, the stock can be graded out of the pickle, and only the stock best suited for sole leather need be used for that purpose. The remaining stock can be split in the pickled state, if desired, and tanned as readily with chrome as with vegetable tanning materials, if that be desired. It has the enormous advantage of bringing all stock into the same physical state. The only precaution that must be taken is to maintain a salt concentration of about 3 per cent in the rocker liquors and in other liquors until the stock has been completely penetrated by tannin, after which the precaution is no longer necessary. In addition, those tanning materials must be avoided that are readily precipitated by acid and salt.

As tanning material, equal parts on tannin basis of cutch, wattle and chestnut can be used. There are available specially treated quebracho extracts, resistant to precipitation by acids and salt; these can be used.

The method of pickling described in Chapter 9 is used. For very heavy steer hides, precautions must be taken to be sure that the stock is pickled to equilibrium, but the regular overnight pickling is usually sufficient to take care of this. The method of tanning in the rockers is exactly the same as that described for bated stock except for the replacement of quebracho by wattle and the requirement that each 100 gals. of rocker liquor contain 25 lbs. of salt. In starting the system, salt must be added to each liquor, but, after that, it is necessary merely to add 25 lbs. of salt to each 100 gals. of new liquor entering the section. For example, in making up the new head rocker liquor daily, when 2300 gals, of the previous headrocker liquor is augmented by 1150 gals. of new liquor, only 287½ lbs. of salt would be added to take care of the 1150 gals, of new liquor. Twenty working days in the rocker liquors should be sufficient for complete penetration by tannin. If it is, the stock can go right into the layer system or into the drum for rapid tanning. If it is not struck through, upon coming from the head rocker, as a safeguard for one not familiar with the tanning of pickled stock, it would be best to keep it in a vat filled with liquor of the same composition, including salt, as that of the head rocker.

In vegetable-tanning pickled steer hides, the tanner should be cautioned that

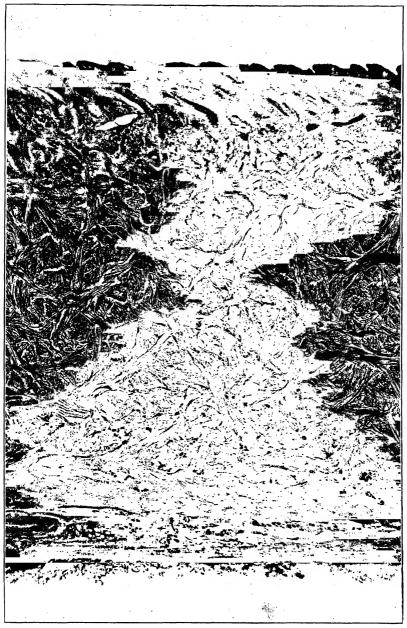


Fig. 187. Vertical Section of Vegetable-tanned Steer Hide for Sole Leather.

Location: butt. Thickness of section: 40 microns, or 0.00158 inch. Magnification: 15 diameters.

excessive percentages of sulfuric acid left in vegetable-tanned leather cause deterioration of the leather upon aging. The process for tanning pickled calfskins described above leaves in the finished leather about 0.6 percent sulfuric acid, or about 1.4 percent on the hide-substance basis. This amount causes no deterioration after aging for more than twenty years, and probably none after any length of time. However, when the content of sulfuric acid is increased above 4 percent, or about 9 percent on hide-substance basis, the leather deteriorates with time.

Bowker showed that sole leather tanned with quebracho alone does not deteriorate with time unless the sulfuric-acid content exceeds 3 percent, or about 6.5 percent on the hide-substance basis, but that leather tanned with chestnut alone may begin to deteriorate when the sulfuric acid exceeds only 1.5 percent, or about 3.4 percent on the hide-substance basis. When the stock comes out of the pickle, it contains about 6.5 percent sulfuric acid on hide-substance basis, but over 80 percent of this is usually lost in the rockers and passes to the sewer.

For the tanner who uses reasonable care in the manufacture of his leather, there is practically no danger of getting too much sulfuric acid into his leather, but he should be acquainted with the facts and have occasional analyses of his leather made as a safeguard. The greater sensitivity of leather tanned with chestnut to acid deterioration may be due to its content of gallic acid, which apparently is destructive and does not appear in a determination of sulfuric acid. The danger of acid deterioration can be lessened by decreasing the proportion of chestnut used or by eliminating it entirely. If the pH value of the leather as determined by the provisional method of the A. L. C. A. is greater than 3.0, the leather can be considered safe against acid deterioration. This determination includes the effect of gallic and every other acid.

Fig. 187 represents a typical cross-section of sole leather after vegetable-tanning, but before being subjected to the many subsequent operations.

Vegetable Tanning Horse Hides

In tanning horse hides, it should be remembered that the horse hide is unique in having unusually dense and tight structures in the butt areas and unusually loose structures in the rest of the hide. Since leathers from these two different areas are used for quite different purposes, it is possible to buy separately as raw stock horse fronts and horse butts. In vegetable tanning, the butts are penetrated by tannins extremely slowly, but the fronts much more rapidly than steer hides. The dense portion of the horse butt is called the shell. The structure of the raw butt is shown in Fig. 32 (p. 53). It is customary to split the shell into two layers and to finish it on the split side. Splitting it before tanning greatly facilitates penetration by the tannin.

Fig. 188 shows a cross-section of vegetable-tanned horse butt, which has already been split through the shell. For comparison, Fig. 189 shows a cross-section of vegetable-tanned horse front. The looseness of structure of the horse front is in marked contrast to the tightness of structure of the shell of the butt. Either fronts or butts may be tanned like sole leather, but less time will be required for the fronts. For the butts, it is desirable to follow the procedure for the rapid tannage of sole leather.

Vegetable Tanning Harness and Strap Leathers

Both steer and cow hides are tanned for harness and strap leathers are tanned much the same as for sole leathers through the rocker sections. After the tannin has completely penetrated the hides, the tannage is not continued so long as for



Fig. 188. Vertical Section of Vegetable-tanned Horse Butt.

Location: butt.
Thickness of section: 20 microns, or 0.00079 inch.
Magnification: 70 diameters.



Fig. 189. Vertical Section of Vegetable-tanned Horse Front.

Location: between shoulder and butt. Thickness of section: 20 microns, or 0.00079 inch. Magnification: 70 diameters.

sole leather, because the same firmness and solidity is not desired. Sometimes the stock is carried through a short layer section. Tanners who make both sole and harness leathers tan all stock alike through the rockers or to the point of complete penetration by tannin and then sort for suitability for sole or harness leather.

Sometimes a section of still vats is used in place of the rocker section. The whole hides are hung over poles and set into the frame in a vat that is not rocked. The head and tail liquors always remain in the same vats, and only the stock is moved progressively through the vats from tail to head. Each working day stock

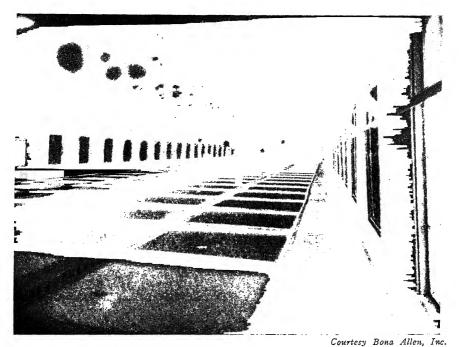


Fig. 190. Harness-leather Yard of Still Vats.

liquor is added to the head vat in proportion to the bated weight of the pack entering the tail vat. Volumes of liquor equal to that added to the head vat press liquor from one vat to another, wasting the same volume of tail liquor to the sewer. Such a series of sections is shown in Fig. 190.

Harness leather lends itself very well to the rapid tannage. After the stock has been completely penetrated by tannin in the rocker liquors, it is taken to the tanning drum. A pack of 1700 lbs. wet weight of leather is put into the drum, covered with 380 gals. of quebracho liquor not bisulfited of 6 percent tannin and run for 8 hours. It is then piled and covered and left for 48 hours. The waste liquor is run to a mixing tank to be strengthened to 6 percent of tannin for reuse. The stock is then covered with 380 gals. of water at 80° F. in the drum and run for one hour. It is then taken out and sent on for the special procedures for making harness leather to be described in Chapter 19. The liquor is run to the mixing tank for making up into new 6 percent tan liquor. Where increased plumpness is desired

in the leather, cutch is used to replace part of the quebracho, the greater the proportion of cutch to quebracho, the greater the plumpness of the leather.

Strap leathers are treated exactly as for sole leather, through the retannage.

Vegetable Tanning Heavy Strap Leathers of Great Strength

When the life of a person may depend upon the strength of a strap, yields of leather and cost of tanning materials become of secondary importance. Very heavy steer hides are used and they are properly delimed and bated after unhairing.

The stock tanning liquor is prepared by dissolving 1000 lbs. of ordinary solid quebracho in water to make a total of 1000 gals., decanting the liquor from the sludge after settling over night, adding to it 2000 lbs. of Plantation gambier extract dissolved in water to make 1000 gals., mixing well, analyzing and adding water to make a stock tanning liquor of 6 percent tannin. Enough lactic acid is added to this stock liquor to reduce its pH value to 3.8. A rocker section is set up exactly as in tanning sole leather. Once the system is in full operation, the amount of stock liquor pressed onto the head rocker per 100 lbs. of bated stock entering the tail rocker should be such as to maintain a tannin strength of 0.5 percent in the tail rocker. The pH value should increase gradually from 3.8 in the head rocker to 5.0 in the tail rocker. If the pH value of the head rocker should rise above 3.8, lactic acid should be added to bring it down to 3.8. If the pH value of the tail rocker should rise above 5.0, enough sulfuric acid should be added to it to bring it down to 5.0. The number of vats required in the rocker section should be such that the stock is completely penetrated by tannin before reaching the head rocker. will increase with the thickness of the stock.

Upon taking the stock from the head rocker, pile it over night and then make up into packs of 1500 lbs. wet weight each. Put a pack into a tanning drum 7 feet wide by 7 feet in diameter, running at 12 r. p. m., and add 300 lbs. of Plantation gambier extract, 50 lbs. of aluminum sulfate and 25 lbs. of salt dissolved in water to make 150 gals. at 70° F. Run the drum for 4 hours and then take out the stock, pile it, cover it and let stand for 48 hours. Then stuff and finish as for strap or harness leathers as described in Chapters 15 and 18.

Vegetable Tanning Miscellaneous Leathers

The procedures given above for vegetable-tanning cover practically every type of leather, and the tanner can find among them at least one that will suit his purpose for tanning any kind of leather. It is unusual to tan goatskins with vegetable-tanning materials, but the calf procedure gives excellent results. Goatskins can be pickled and tanned like sheepskins, but the tanning time may have to be extended. Very heavy hides require a long time to effect complete penetration by the tannin, and it is important to remember that the tannin can completely penetrate through the thickness of a hide and yet not reach all of it to combine with it to form leather. The tannin must not only penetrate through the thickness of a hide, but it must penetrate into the collagen jelly of which the fibrils of the hide are composed. This is one reason why the tanning time must often be extended long beyond that necessary for complete penetration through the thickness of the hide.

The use of other tanning materials to assist in vegetable tanning will be discussed in Chapter 13.

Diffusion of Tannin into Hides

In penetrating a hide, the tannins diffuse first into the spaces between the fibers and then into the collagen jelly of which the fibrils are composed. In order

to get a better understanding of this latter type of diffusion, studies have been made of the diffusion of tanning materials into gelatin jelly. Hoppenstedt noted that different tanning extracts diffused into gelatin jelly at different rates, the order of increasing rate of diffusion being mangrove bark, quebracho, hemlock bark, algarobilla, valonia, oak bark, myrobalans, chestnut wood, gambier, divi-divi, and sumac. This is roughly the order of decreasing astringency. He repeated the test, using gelatin jelly containing ferric ammonium alum. The iron salt gives a dark coloration with both tannins and certain non-tannins and serves to make the degree of penetration more sharply defined. The order of diffusion appeared to be roughly the same whether or not the iron salt was present. It was, of course, the extent of penetration by certain non-tannins that was measured, as these diffuse more rapidly than the tannins.

Later Thomas carried this work further. He prepared a 5-percent dispersion of gelatin in hot water containing 0.1 percent ferric chloride and poured it into a series of test tubes to three-quarters of their capacities. When the dispersions had set to jelly, equal volumes of solutions of different tanning extracts were poured on top of the jellies, which were then kept in an ice box. All of the extracts were made to contain 1 percent of dry solid matter. At intervals he noted the depth of penetration as indicated by the coloration of the ferric chloride. The rate of diffusion for different materials increased in the following order: quebracho, hemlock bark, larch bark, oak bark, chestnut wood, gambier, and sumac, agreeing with the results obtained by Hoppenstedt. This is roughly also the order of increasing ratio of non-tannin to tannin in the extracts. In 96 hours the gambier, which had the highest ratio of non-tannin to tannin, penetrated to a depth of 18.0 millimeters as against only 4.8 millimeters by the quebracho, which had the lowest ratio.

The fact that mangrove bark (or cutch extract) penetrates gelatin jelly less rapidly than any other extract agrees with the writer's finding that it also penetrates steer hides less rapidly than other extracts. However, it is interesting to note the slow penetration of quebracho into the jelly in contrast to its rather rapid penetration through the thickness of a steer hide.

Tests by the writer showed that the rate of penetration increases with the concentration of the tanning extract. Since Thomas used the same concentration of total solid matter in all tests, he had a higher concentration of non-tannin and a lower concentration of tannin where the ratio of non-tannin to tannin was higher, as in gambier. The measurements were really those of the diffusion of non-tannins because they are colored by contact with ferric chloride and they diffuse at a greater rate than the tannins. This offers one explanation of the findings. It is corroborated by the work of Mezey, who sought to measure the penetration of the tannin into calf skin.

Mezey immersed strips of bated calf skin in solutions of tanning extracts of various strengths and for various intervals of time. Pieces were then cut from the central part of the strips, rinsed with water, and placed in a microtome. Sections were cut and stained with potassium dichromate, which gives a dark coloration with the tannins. The stained sections were dehydrated, mounted in balsam, and the penetration of the tannins measured with a micrometer. With solutions containing 1 percent of total solid matter and immersion for 4 hours, the rate of penetration increased in the following order: mangrove, sumac, quebracho, chestnut, sulfited quebracho. Sumac actually penetrated to a lesser extent than quebracho. However, Mezey was measuring the penetration by tannin rather than non-tannin and, since the concentration of tannin was higher in the quebracho solution than in the sumac solution, an explanation is afforded of the greater rate

of penetration of tannin from the quebracho solution which is in line with the explanation given above in the gambier-quebracho experiment. However, this explanation does not hold for the behavior of the other materials in Mezey's experiment. The cause of the difference in rate of diffusion by different materials is evidently more complicated. Mezey himself points out that other important factors are the pH value, degree of dispersion of the tanning material, temperature, and tanning conditions.

Wilson and Kern extended Thomas' experiments to show the effect of pH value. They treated a large volume of a dispersion of gelatin in dilute ferric chloride solution with tartaric acid until its pH value was reduced to 2.5, as determined by the hydrogen electrode. Equal portions were then treated with sodium hydroxide to give the desired pH values, which ranged from 2.5 to 11.0. Dilutions were such that the final dispersions contained 5 percent of gelatin and 0.1 percent of ferric chloride, as in the experiments of Thomas.

Solutions of gambier and quebracho extracts were treated with tartaric acid to give a pH value of 2.5. Equal portions were then treated with sodium hydroxide to give series of pH values the same as in the series of jellies. Each final liquor contained 1 gram of solid matter of the original extract per 100 cubic centimeters.

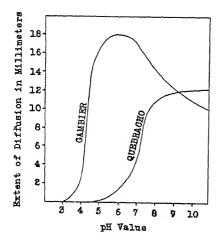


Fig. 191.

Rates of Diffusion of Gambier and Quebracho into Gelatin Jelly as a Function of pH Value.

The gelatin dispersions were poured into test tubes and allowed to set. Onto each was poured a given volume of tan liquor having the same pH value as the jelly. They were kept in a refrigerator and examined at intervals for 96 hours. Although pH values above 5.0 are not ordinarily used in vegetable tanning, a range of 2.5 to 11.0 was used to show the continuity of the results. The extents of the diffusions in 96 hours are shown in Fig. 191.

The effect of pH value is really very great. Gambier penetrates very rapidly as the pH value is raised above 3.0, but quebracho does not penetrate measurably until the pH value is raised above 4.7.

The effect of pH value upon the penetration of the cutch-chestnut-quebracho mixture into steer hide shown in Table 36 (p. 298) is interesting to study in connection with this work.

In all the experiments described above, where the rate of diffusion of one tanning material was compared with that of another, the variable factors did not have identical values. This must be taken into consideration in drawing any conclusions. The rate of diffusion is actually a function of a number of variables, including pH value, temperature, concentrations and kinds of tannins and non-tannins, and thickness and previous history of the skin.

Distribution of Tannin Through Thickness of Leather

In practice, complete saturation of the protein with tannin is rarely, if ever, accomplished. In the ordinary methods of tanning this would require many months and might prove undesirable, if accomplished. The surface of the skin is in contact with the tannin for a considerably longer period of time than the middle portion

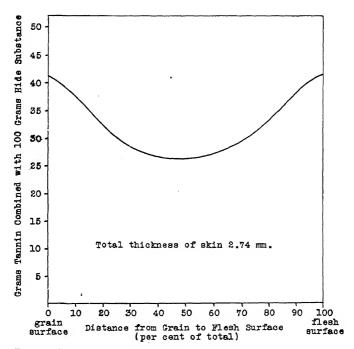


Fig. 192. Distribution of Combined Tannin throughout Thickness of Calfskin after Tanning for Ten Days.

and, consequently, is always more heavily tanned. This is further accentuated by the fact that the liquor finally reaching the interior is more dilute than that at the surface, having lost some of its tannin through combination with protein on the way. If the difference in degree of tannage of the surface and interior regions is very great, the skin will either be distorted or else the grain surface will break up into coarse wrinkles upon bending the leather inward, which is undesirable. The reason for this is that the area of the layers tends to increase with the degree of tannage, giving the grain layer a greater area than the middle layer.

The uniformity of distribution of tannin can be increased by increasing the rate of diffusion and decreasing the rate of fixation of tannin. The commonest method of doing this is to use the same liquor repeatedly, with the necessary strengthening, until the ratio of non-tannin to tannin becomes relatively high. Tannins and certain

non-tannins form compounds with collagen, but the collagen-tannin compounds are very stable, while the collagen-non-tannin compounds are considerably dissociated. The non-tannins, having a much smaller molecular weight than the tannins, diffuse more rapidly into the skin. When the slowly moving tannin reaches a point where it would combine with collagen, it cannot do so because the point is already occupied by non-tannin. Tannin that would otherwise have combined with collagen near the surface of the skin is thus enabled to proceed into the interior and the measured rate of penetration is thereby increased. This action is more marked the greater the concentration of non-tannin capable of combining with collagen. The collagen-tannin compound being much the more stable, tannin replaces non-tannin as fast as the collagen-non-tannin compound hydrolyzes.

Greater uniformity of distribution can also be brought about by the proper adjustment of pH value, temperature, and concentrations of the important constituents of the tan liquor, but this requires considerable experience to guarantee against damage to the stock.

Since absolute uniformity of distribution of tannin throughout the skin is not practical, it is important to know what differences in tannin content are permissible. Fig. 192 shows the distribution of combined tannin throughout the thickness of a calf skin which was tanned for ten days in a series of liquors made from blended extracts. After tanning, before drying, the leather was split into a number of layers and each was then dried and analyzed separately in the author's laboratories. The combined tannin was taken as the difference between 100 percent and the sum of the percentages of water, fat, collagen, matter soluble in water, acid, and insoluble ash. The middle portion of the skin has only about two-thirds as much combined tannin as the surface layers, but this distribution is entirely satisfactory as shown in the properties and appearance of the leather. How great the discrepancy must be before the leather is spoiled has not yet been determined with accuracy, but the writer believes that the degree of tannage in the middle of the skin should be at least half as great as at the surface to insure a leather having a grain of reasonably fine "break."

Effect of Time and Concentration of Tan Liquor upon Tannin Fixation

It is practically impossible to measure the true *rate of fixation* of tannin by using a whole thickness of hide because the *rate of diffusion* of the tannin into the hide influences the observed results. However, the influence of diffusion rate can be minimized by using hide powder instead of a whole thickness of hide. Comparisons of the tanning of both hide powder and of whole hide under the same conditions often give interesting information of the effect of diffusion rate.

Thomas and Kelly carried out a very important series of experiments on the fixation of tannin by hide powder. Their tan liquors were centrifuged and filtered and only the clear filtrates used in the experiments. The use of filtered liquors with hide powder gave results which were more uniform and which probably represent actual tanning conditions more closely, since the surfaces of the whole skin act as filters, permitting only the soluble matter to come into contact with the great bulk of the skin protein.

Portions of purified hide powder equal to 2 grams of anhydrous substance were shaken with 100 cubic centimeters of tan liquor of the desired concentration and for fixed intervals of time. The powder was then washed until the wash water no longer gave a dark color upon the addition of a drop of ferric chloride solution. (It was found that the ferric chloride test is capable of detecting 1 part in 75,000 of either gallic acid or pyrogallol.) The powders, freed from soluble matter, were

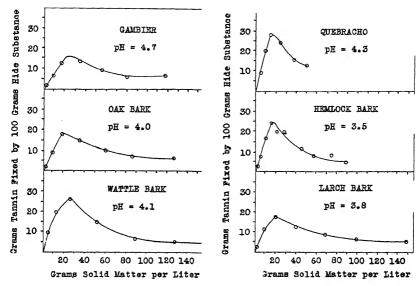


Fig. 193. Rate of Fixation of Tannin by Hide Powder as a Function of Concentration of Tan Liquor. Tanning time, 24 hours.

dried in a current of warm air and then completely dried in the oven. The increase in weight of the absolutely dry material was taken as the amount of tannin fixed by 2 grams of hide powder.

Fig. 193 shows how the rate of tannin fixation varies with concentration of solutions of quebracho, hemlock-bark, larch-bark, gambier, oak-bark and wattle-bark extracts. A solution of 120 grams per liter is practically the same as one of one pound per gallon. With increasing concentration, the fixation increases to a point of maximum and then decreases with further increase in concentration. The

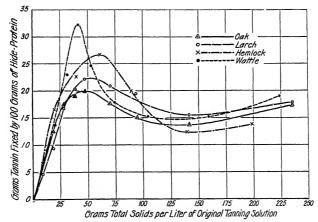


Fig. 194. Rate of Fixation of Tannin by Defatted Hide Powder as a Function of Concentration of Tan Liquor at pH Value of 5.0. Time, 24 Hours.

points of maximum occur at strengths less than those normally found in sole-leather yards. This means that when the liquors are strengthened, the rate of tannin fixation actually decreases, but we know that the rate of diffusion is increased because the tannins penetrate hides more rapidly from stronger liquors.

This explains why early attempts to tan sole leather rapidly by using very strong liquors resulted in leather of low yields. The secret of success lies in using the strong liquors merely to effect rapid and complete penetration and then to use weak liquors to bring about higher fixation of tannin.

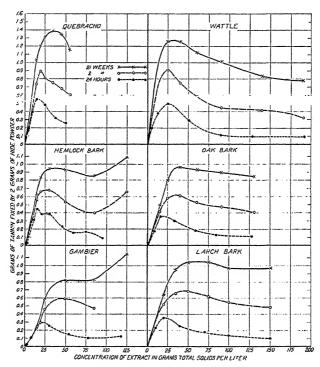


Fig. 195. Fixation of Tannin by Defatted Hide Powder as a Function of Concentration of Tan Liquor at pH Value of 5.0 for Different Periods of Time.

Thomas and Kelly carried out another series of experiments, using defatted hide powder freed from the portion that would pass a 100-mesh sieve. Five-gram portions of dry powder were kept in contact with 100 cc. of the tan liquor for 24 hours. The pH value of each tan liquor was adjusted to 5.0 by the addition of sodium hydroxide. The percent of tannin in the total solid matter of each extract used was determined by the Wilson-Kern method of tannin analysis and found to be as follows: oak-bark 20.6, larch-bark 20.6, hemlock-bark 27.2, and wattle-bark 30.4. The results of the experiment are shown in Fig. 194.

Thomas and Kelly then measured the effect of time by setting up another series of experiments, using 2 grams of purified hide powder and 100 cc, of tan liquor with pII value adjusted to 5.0. The effects of concentration for tanning periods of 2 weeks and 21 weeks are shown in Fig. 195. The curves for 1 day taken from

Fig. 193 are included for comparison, but it must be remembered that they represent results where no adjustments of pH value were made.

With a tanning time of 21 weeks, the points of maximum become less sharp, showing that increasing the strength of a tan liquor slows up the *rate* of fixation, but apparently not the ultimate amount fixed, if time enough is allowed.

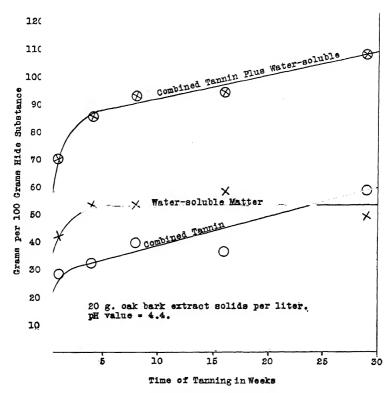


Fig. 196. Continued Fixation of Tannin by Bated Calfskin for 29 Weeks from Oak-bark Extract Solution.

Merrill, working at the time in the writer's laboratories, measured the fixation of tannin by bated calfskin as a function of time. He used a solution of oak-bark extract containing one pound of total solids per 6 gallons, maintaining this concentration by the necessary additions of fresh extract during the tanning period of 29 weeks. Samples of the leather were taken at intervals for analysis of combined tannin, water-soluble matter and hide substance. The progress of the tanning is shown in Fig. 196. It is interesting to note the steady increase in combined tannin, even after nearly seven months of tanning.

Effect of pH Value on Fixation of Tannin

Thomas and Kelly next turned their attention to the effect of pH value upon the fixation of tannin by hide powder. The procedure used was the same as that used in their studies of the effect of concentration. In each case, the pH value of the tan liquor was adjusted to the desired value by the addition of caustic soda or hydrochloric acid. Figs. 197 and 198 show the results for quebracho, gambier, oakbark, wattle-bark, hemlock-bark and larch-bark extracts.

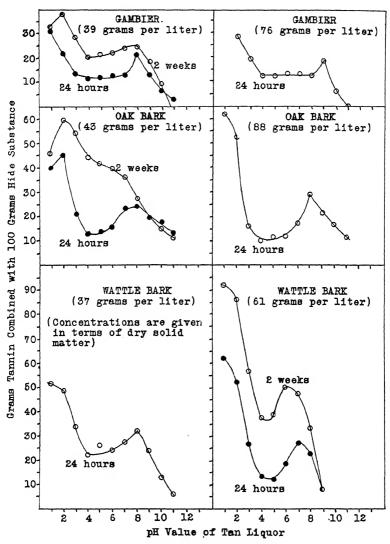


Fig. 197. Fixation of Tannin by Hide Powder as a Function of pH Value of Liquors of Different Extracts.

Although the practical interest of most tanners is only in the pH range from an extreme low of about 2.5 to an extreme high of about 5.5, results outside of this range are of great theoretical significance, and some day they may assume real practical importance. For the present, the practical importance to the tanner lies

in the fact that minimum fixation of tannin occurs for all materials at pH values between pH values of 4 and 5, and that sharp increases in tannin fixation occur when the pH value is dropped below 4. Values for "grams tannin combined with

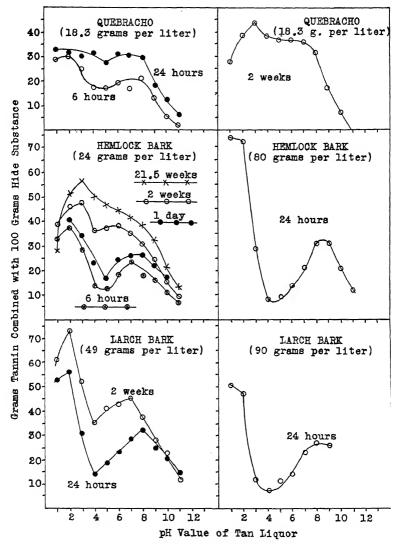


Fig. 198. Fixation of Tannin by Hide Powder as a Function of pH Value of Liquors of Different Extracts.

100 grams hide substance" correspond to the "fixation value" discussed in Chapter 10.

The marked tanning action that takes place at pH values above 7 is attributed to materials present in vegetable-tanning extracts that are similar to quinone,

which has been used to tan hides in alkaline liquors. So far as the writer knows, quinone has not come into practical use as yet, although he has used it as the only tanning agent in making some satisfactory calf leather that had the properties of vegetable-tanned leather, with the added advantage of being unaffected by boiling water.

Effect of Kind of Acid Added on Tannin Fixation

The question has often been raised as to whether or not it makes any difference what kind of acid is used in lowering the pH value of tan liquors. In lowering the pH value of a liquor from 5 to 3, only a very small proportion of a strong acid, such

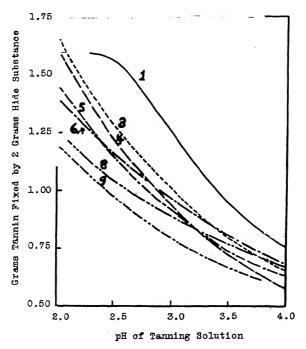


Fig. 199. Effect of Kind of Acid Added upon Wattle-bark-tannin Fixation by Hide Powder as a Function of pH Value. Tanning time, 6 hours.

- 1. acetic acid.
- lactic acid.
- 4. formic acid.
- 5. citric acid.
- 6. tartaric acid.
- 8. oxalic acid.
- 9. hydrochloric acid.

as hydrochloric, is required, but a very much larger proportion of a weak acid, like acetic, is required. Although the tan liquors may be brought to the same pH value, the total quantity of acid added does have an effect, as shown by the work of Thomas and Kelly.

They placed portions of purified hide powder equal to 2.000 grams of collagen in 450-cc. rubber-stoppered bottles and allowed them to soak in 50-cc. portions of distilled water for one hour. Then 350-cc. portions of wattle-bark solution were

added. There had previously been added to the tannin solutions sufficient percentages of the various acids studied to yield the desired pH values of the tan liquors after contact with the wet hide powders. The concentration of tanning agent was such as to provide 40 grams of total solid matter per liter when diluted with the water already in contact with the hide powder. These mixtures were then agitated in a tumbling machine at room temperature for 6 hours in one series, and for 24 hours in the other, after which they were filtered through Wilson-Kern extractors. In every case the filtrate gave a positive gelatin-salt test for tannin, showing that in no case was the tannin content of the solution reduced to zero. The tanned powders were washed with distilled water until the wash water gave no color

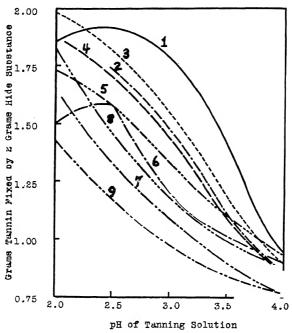


Fig. 200. Effect of Kind of Acid Added upon Wattle-bark-tannin Fixation by Hide Powder as a Function of pH Value. Tanning Time, 24 hours.

- 1. acetic acid.
- 2. succinic acid.
- 3. lactic acid.
- 4. formic acid.
- 5. citric acid.

- ο.
- 6. tartaric acid.
 - 7. chloracetic acid.
 - 8. oxalic acid.
 - 9. hydrochloric acid.

with ferric chloride. They were then air-dried and then dried completely in a vacuum oven at 100° C. The increase in weight of the dried powders was taken as the value for tannin fixed. The results are shown in Figs. 199 and 200.

The effect of kind of acid is very striking. The general order of increasing effect of the various acids upon tannin fixation is hydrochloric, monochloracetic, oxalic, tartaric, citric, formic, succinic, lactic and acetic acids. In other words, the weaker the acid, the greater is its effect when used alone to lower the pH value

of the tan liquor. The weaker the acid, the greater will be the percentage required to produce a given lowering of pH value.

Effect of Neutral Salts on Tannin Fixation

Thomas and Kelly also studied the effect of adding common salt (sodium chloride) or of Glauber's salt (sodium sulfate) to tan liquors of gambier and hemlock-bark extracts upon the fixation of tannin by hide power. In each test, 100-cc. of tan liquor, a weighed amount of salt, and the equivalent of 2 grams of water-free hide powder were put into a bottle and shaken, in a rotating box, for 24 hours. The contents were then transferred to a Wilson-Kern extractor, filtered, and washed until the washings gave no coloration with ferric chloride solution. The tanned powders were then dried in a vacuum at 100° C. and weighed, the increase in weight of the dry powder being taken as tannin fixed.

In order to guard against including as fixed tannin any matters rendered insoluble by the added salt, blanks were run leaving out the hide powder and corrections were made where necessary.

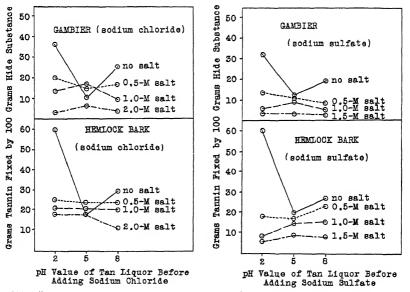


Fig. 201. Effect of pH Value and Added Sodium Chloride or Sodium Sulfate upon Fixation of Tannin by Hide Powder from Gambier and Hemlock-bark Liquors.

The insoluble matter of the extracts was first removed by centrifuging strong solutions, which were then diluted to contain 40 grams of solid matter of the tanning extract per liter, after adjusting the pH value to 2, 5, or 8, by addition of hydrochloric acid or sodium hydroxide.

The results are shown in Fig. 201.

1.0M sodium chloride means about 0.49 lb. of common salt per gal. of liquor. 1.0M sodium sulfate means about 1.18 lbs. of anhydrous Glauber's salt per gal. of liquor. 0.5M means one-half as much as 1.0M, and 2.0M means twice as much.

The amount of common salt used in the vegetable tanning of pickled stock is equal to about 0.5M sodium chloride. The effect of adding this amount of

salt is to lessen the effect of pH value sharply as compared to the effect where no salt is used. When vegetable tanning unpickled stock, the pH value decreases from about 5.0 in the tail stick liquor to about 3.5 in the head handler liquor.

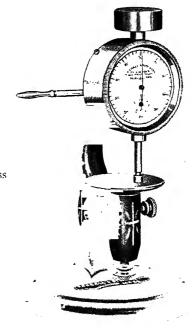


Fig. 202. Randall & Stickney Thickness Gauge for Leather and Raw Skin.

Courtesy Frank E. Randall

When tanning pickled stock, the pH value increases from about 2.7 in the tail stick liquor to about 3.5 in the head handler liquor. The effect of adding the salt is to increase the tannin fixation at a pH value of 5.0 and to decrease it at a pH value below 4.0. Glauber's salt is much more effective than common salt in decreasing the fixation of tannin.

Table 40. Plumping of Calfskin by Tan Liquor Containing 0.21 lb. Oak-bark Extract per Gallon and Lactic Acid and Salt (Sodium Chloride) as Shown.

—Moles per Liter †— Lactic Sodium		Gauge Readings in MM.———————————————————————————————————			Final pH Value
acid	chloride	Initial	Final	Ratio *	at 25° C.
None	None	1.346	2.150	1.60	4.63
0.0025	"	1.411	2.343	1.66	3.94
0.0050	"	1.383	2.699	1.95	3.74
0.010	46	1.433	3.842	2 68	3.47
0.025	"	1.470	4.564	3.10	3.05
0.050		1.360	4.497	3.31	2.81
0.100	"	1.434	5.100	3.56	2.52
	0.05	1.456	4.522	3 11	2.49
	0.10	1.458	3.918	2.69	2.47
	0.25	1.461	3. 4 83	2.38	2.43
	0.50	1.420	2.182	1.54	2.37

^{*}This is a measure of the degree of plumping.
†One mole lactic acid per liter is the same as 0.75 lb. of pure acid per gal. and one mole sodium chloride per liter is the same as 0.49 lb. of common salt per gal.

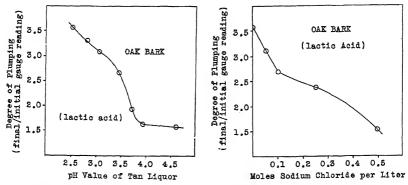


Fig. 203. Effect of pH Value and of Added Salt upon the Plumping of Calfskin in Oak-bark Liquors.

Effect of pH Value and Added Salt on the Plumping of Stock in Tan Liquors

Tanners of sole leather usually like to produce leather as plump as practical. They have found that increasing the plumpness in the tan liquors usually results in a plumper final product, although the end result is influenced in large measure by the treatment of the stock after it leaves the layer section. Tanners of flexible leathers requiring very great strength usually avoid excessive plumping.

In Chapter 9, there was described a method developed by Wilson and Gallun for measuring degrees of plumping and falling of raw stock as a function of pH value. They used this method for determining the effect of pH value and of added common salt upon the plumping of calfskin in oak-bark liquors.

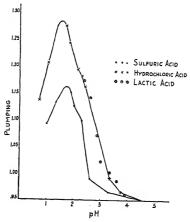


Fig. 204. Effect of pH Value as Produced by Different Acids upon the Plumping of Cowhide in Wattle-bark Liquors.

For this experiment a piece was selected from the butt of a calfskin, after liming, unhairing, and washing, of as nearly uniform thickness as possible and cut into squares having a side of about 2 centimeters. These were delimed by washing with several changes of 0.01M hydrochloric acid containing 10 percent of sodium

chloride, then kept over night in a saturated solution of sodium bicarbonate containing 10 percent of sodium chloride, washed thoroughly, and finally bated for 5 hours at 40° C. in a solution of 1 gram per liter of pancreatin, having a pH value of 7.6. The pieces were then washed for 24 hours in running tap water and were kept under distilled water in a refrigerator at 7° C. until used. The resistance to compression of each piece of skin was measured by means of a Randall & Stickney thickness gauge with a flat, metal base, upon which the piece of skin was

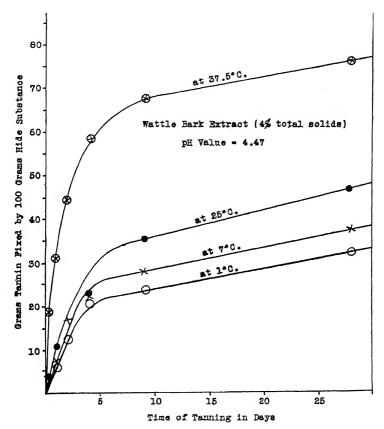


Fig. 205. Effect of Tanning Time upon Fixation of Tannin by Hide Powder from Wattle-bark Liquors at Different Temperatures.

placed, and a plunger, having a circular base 1 square centimeter in area, capable of pressing on the surface of the skin under constant pressure. The gauge reading was taken, in every case, exactly two minutes after dropping the plunger onto the skin.

The Randall & Stickney gauge is shown in Fig. 202. Eleven tan liquors were prepared as indicated in Table 40. The gauge readings of pieces of the standard skin were taken and they were then shaken with water to bring them back to their normal shape, after being compressed in the gauge. They were then put into the tan liquors and allowed to remain there for 24 hours at 20° C. The final gauge

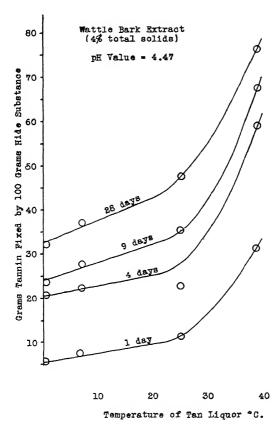


Fig. 206. Effect of Temperature upon Fixation of Tannin by Hide Powder from Wattle-bark Liquors for Different Tanning Periods.

readings were then taken. In each case 3 pieces of skin were put into 100 cubic centimeters of tan liquor and the agreement between the triplicate determinations was satisfactory. The degree of plumping caused by the liquor is measured by the ratio of the final to the initial gauge reading.

The results are shown in Table 40 and in Fig. 203.

As the pH value was decreased below 4 in the absence of salt, the plumping became inordinately high and the untanned middle layers of the skins became gelatinized and destroyed; but in the presence of 0.25 lb. of salt per gal. (0.5 mole per liter), there was slightly less plumping at a pH value of 2.37 than there was at a pH value of 4.63 with no added salt. The general effect of adding acid to tan liquors is to increase plumping and that of adding salt is to decrease plumping.

Page and Gilman used the Wilson-Gallun method to measure the effect of adding acid upon the plumping of cowhide in wattle-bark liquors. The tan liquors contained 0.21 lb. of wattle-bark solids per gal. and the tanning time was 24 hours. The results are shown in Fig. 204 as a function of pH value produced by adding sulfuric, hydrochloric or lactic acid.

As the pH value is decreased below 3.5, that often found in layer and handler liquors, plumping increases at an inordinate rate to a pH value of about 2, below which the plumping falls off again. Although lactic acid is much weaker than hydrochloric acid, the plumping produced is the same for each. Counting the effect of the acid as the additional plumping over unity, it will be seen that sulfuric acid produces only about one-half as much additional plumping as does either lactic or hydrochloric acid. Sulfuric acid is a dibasic acid and lactic and hydrochloric acids are both monobasic. The findings are in agreement with the fundamental rule that monobasic acids produce about twice as much swelling of protein jellies at the same pH value as do dibasic acids.

Effect of Temperature on Tannin Fixation

Most tanners know that hides and skins tan very slowly in cold liquors. In the experiments described above, where no temperatures are mentioned, it means that they were conducted at room temperature, about 70° F. Thomas measured the effect of temperature upon the fixation of tannin by hide powder from solutions containing one-third pound per gallon of solids of wattle-bark extract. The results

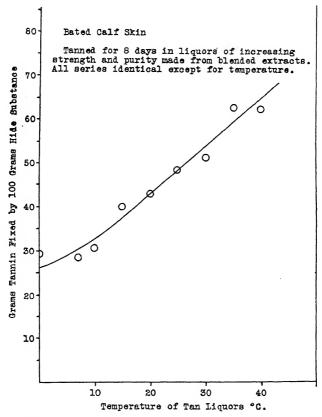


Fig. 207. Effect of Temperature upon Fixation of Tannin by Calfskin from Regular Yard Liquor in 8 Days.

for tannin fixed as a function of time for different temperatures are shown in Fig. 205. The results for tannin fixed as a function of temperature for different tanning periods are shown in Fig. 206.

Merrill carried out a similar experiment with the tanning of bated calfskin in the regular yard liquor. The results are shown in Fig. 207.

Increasing the temperature of the tan liquor from 50° F. (10° C.) to 95° F. (35°C.) has caused the percentage of tannin fixed in 8 days to double. This is deserving of much careful thought by the tanner. Every precaution should be taken in the winter to keep the temperature of the liquors above 70° F., and it is very important to keep the temperatures the same at all times of the year, if uniform tanning is to be expected.

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Chapter 12

Chrome Tanning

Just as the bulk of all heavy hides today are converted into leather by means of vegetable tanning, so the bulk of all light hides and skins are converted into leather by means of chrome tanning. Although vegetable tanning was developed many thousands of years ago, chrome tanning was developed within the past century. In contrast to vegetable-tanning materials, which are of vegetable origin, chrome-tanning materials are of mineral origin.

The basic material from which chrome-tanning materials are made is an ore, called chromite, which is found chiefly in Asia Minor, but also in the western United States. It consists chiefly of a compound of about 68 percent chromic oxide and 32 percent ferrous (iron) oxide. Kinney described the manufacture of sodium dichromate from this ore as follows: The chromite is ground to a powder and mixed with powdered lime and sodium carbonate. The mixture is heated in a flatbed, reverberatory furnace at from 1500 to 2000° F. for from 6 to 8 hours. During this time, it is raked and turned to facilitate oxidation of the chromic oxide to chromate. It is then cooled and leached with water to extract the sodium chrom-The solution is filtered from the insoluble mass containing the iron oxide. The solution is then concentrated, acidified with sulfuric acid to form sodium dichromate and then further concentrated until the bulk of the sodium sulfate formed is precipitated. The clear liquor is then decanted from the sodium sulfate and further concentrated. It is then cooled and the sodium dichromate is allowed to crystallize out in very pure form. Sodium dichromate consists of red, triclinic crystals that are freely soluble in water. By itself, it has no true tanning properties, but it is readily converted into basic chromium salts, which combine vigorously with hide protein, converting it into very durable leather.

The first concept of chrome tanning has been attributed to Knapp, who, in 1858, described a method for tanning skins with salts of chromium, iron and aluminum. So far as the writer knows, Knapp was not successful in producing chrome-tanned leather commercially. Chrome tanning, as a commercial process, really dates from the patents of Augustus Schultz, of New York, in 1884. In Schultz's process, the skins, after deliming and bating, were tumbled in a solution of potassium dichromate and hydrochloric acid until the dichromate had completely penetrated the skins, after which they were horsed or piled and allowed to drain. They were then tumbled in a solution of hypo (sodium thiosulfate), acidified with hydrochloric acid, which reduced the dichromate to chromic salt, in which condition it combines vigorously with the skin protein, yielding a very stable leather. This process, with modifications, is still in use today under the name of the two-bath process, so named because the stock was first treated with a bath of sodium dichromate and then with a bath of hypo and acid.

In 1893, Martin Dennis patented a process for tanning skins directly in a solution of basic chromic chloride along the lines suggested by Knapp in 1858. Because this was done in a single bath, it came to be known as the *one-bath* process. Today, most chrome tanning is done by the one-bath process, but basic chromic sulfate

has displaced the chloride because it greatly facilitates tanning and produces much better leather.

Making One-bath Chrome Liquors

Although many excellent one-bath chrome-tanning materials are available on the market, many tanners purchase sodium dichromate and prepare their own one-bath liquors. In order to reduce sodium dichromate to the chromic salt that has tanning properties, it is necessary to use a reducing agent (see Glossary). Although there are thousands of different materials that may be used as reducing agents, the two kinds most widely used are sugar and sulfur dioxide. The use of each will be described in turn.

In 1897, Procter described the use of glucose in reducing sodium dichromate to chromic salt and the principle is still in wide use. A common method today is as follows: A wooden tank of about 1200-gals, capacity is lined with lead and equipped with a bottom outlet and with a mechanical stirring device. Into this tank, dump 1000 lbs. of sodium dichromate and add water at 120° F. to make a total volume of 1000 gals. Run the stirrer continuously and add 883 lbs. of 66° Baumé sulfuric acid. Then add very slowly 500 lbs. of 40° Baumé corn syrup. During the addition of the syrup, a violent reaction takes place and the liquor boils, giving off steam and pungent reaction products. The speed of adding the syrup must be so controlled that the reaction does not become too violent. After all the syrup has been added, which may take several hours, allow the solution to cool and age it for several days. Then dilute with water, if necessary, to make a final volume of 1000 gals, and it is then ready for use. After the reaction has been completed, it is customary to pump the liquor to a storage tank for the aging so that the equipment may be kept in continuous use. Immediately after a chrome liquor is made up, chemical changes are still taking place in the liquor and erratic results may be obtained if the liquor is used before these changes are practically complete. For this reason, the liquor is aged; that is, kept until the chemical changes are completed, which may take several days.

This liquor is known as one of 50 percent basicity or of 50 percent acidity of the chromium complex. A solution of pure chromic sulfate has an acid reaction because it reacts chemically with water, forming basic chromic sulfate and free sulfuric acid. If the liberated sulfuric acid is neutralized by adding alkali, more of the sulfate will be converted into free sulfuric acid and the chromic sulfate becomes increasingly basic. Pure chromic sulfate is referred to as having a 100 percent acidity of the chromium complex and 0 percent basicity. When 25 percent of all of the acid that it can liberate has been neutralized, it is called 25 percent basic or 75 percent acidic. The basicity and acidity are so related that 100 percent minus percent basicity equals percent acidity; conversely, 100 percent minus percent acidity equals percent basicity.

The vigor of the combination of chromium with the hide protein increases with increasing basicity up to about 663 percent basicity (or 33½ percent acidity). When the chromic salt is made more basic than this, the chromium precipitates and then can no longer react with the hide protein.

The greater the *acidity* of the chromic sulfate, the more rapidly does it penetrate into the hide; but the greater the *basicity*, the more vigorously does it combine with the hide protein, provided the basicity is not increased to the point where precipitation takes place. In making chrome liquors, it is customary to make the initial *basicity* somewhere between 33½ and 50 percent. The greater the basicity, the less the amount of alkali required in tanning. Generally the chromic

salt that combines with the hide protein has a basicity of about 66% percent, but this can be increased by further neutralization after the leather is tanned. In the foregoing procedure for making chrome liquor, if the amount of sulfuric acid added is increased, the chromic sulfate formed will be less basic. The rule to follow is to *increase* the amount of acid added by 10.59 lbs. per 1000 lbs. of sodium dichromate for each 1 percent that the basicity is to be *lowered*.

In the reaction, as the sodium dichromate is *reduced* to basic chromic sulfate, the sugars of the syrup become *oxidized* and changed to carbon dioxide and a number of different kinds of organic acids. These organic acids combine vigorously with the chromic sulfate to form exceedingly complex chemical compounds, which *greatly* modify the tanning action of the liquor.

Every variation made in details of making the chrome liquor causes a variation in kinds and amounts of the different organic compounds produced, and each such variation thus causes a marked change in the tanning properties of the liquor. Sometimes the change may be found very beneficial and sometimes quite harmful. For this reason, great care must be exercised to keep every factor constant in making chrome liquors this way to insure constancy of tanning properties. Many tanners experiment with the variable factors until they secure the liquor that they believe best adapted to their purposes, and then adhere rigidly to the procedure developed and usually guard it as a secret.

When sulfur dioxide is used in place of sugars, the making of chrome liquor is very greatly simplified, and it is much easier to produce liquors that have exactly the same properties from batch to batch. However, the judicious use of salts of organic acids in chrome tanning results in plumper and fuller leather, which will be discussed later. Such salts are present in liquors made with sugars, but not in those made with sulfur dioxide, which explains why some tanners have obtained plumper leather with the sugar liquors. However, it is so difficult to control the kinds and amounts of organic acids formed when making sugar liquors that the writer has found it preferable to make the liquors with sulfur dioxide and then to add the specific kinds and amounts of salts of organic acids to get the desired properties in the leather.

Of the solutions of the three materials, sodium dichromate, sulfuric acid and sugars, any one can be added to the other two; and in each case a liquor of different properties is obtained because of the different kinds and amounts of organic acids produced.

Sulfur dioxide is made by burning pure sulfur in air. It is a colorless gas of pungent and characteristic odor. It is easily liquefied by the application of pressure, and it is shipped as liquid under pressure in steel drums or tank cars.

Table 41. Relation of Pressure, Specific Volume and Specific Weight of Sulfur Dioxide to Temperature.

Temperature (°F.)	Pressure (lbs. per sq. in.)	Specific Volume (cu. ft. per lb.)	Specific Weight (lbs. per cu. ft.)
0	- 9	0.010820	92.3
14	0	0.010960	91.2
20	2.5	0.011025	.90.5
30	7.0	0.011140	89.6
40	12.4	0.011260	88.9
50	18.8	0.011380 -	87.9
60,	26.2	0.011500	86.9
70	34.9	0.011626	86.0
80	45.0	0.011760 .	85.0
90	56.6	0.011896	84.0
100	69.8	0.012037	83.0

The relations of pressure, specific volume and specific weight to temperature are given in Table 41.

For making small tests, liquid sulfur dioxide can be obtained in cylinders containing from 5 to 150 lbs. For large-scale operation, it is much more economical to purchase it in tank-car lots. Fig. 208 shows the type of storage tank used by

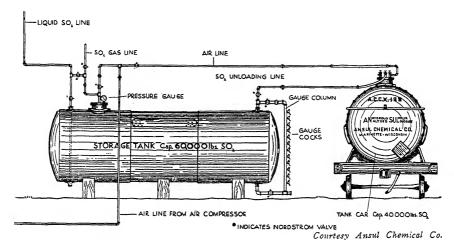


Fig. 208. Showing Method of Transferring Liquid Sulfur Dioxide from Tank Car to Storage Tank.

a number of tanneries and the method of unloading a tank car. The storage tank is of special design to guard against leakage. It is a welded tank measuring 6 feet in diameter by 28 feet long and has a working capacity of 60,000 lbs. of sulfur dioxide. This size permits the complete unloading of a car when there is still a balance of from 10,000 to 20,000 lbs. of sulfur dioxide left in the storage tank. The storage tank is tested at 200 lbs. working pressure and 300 lbs. hydrostatic

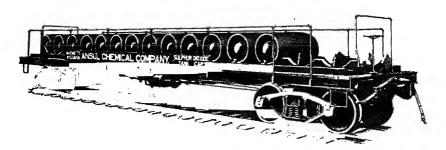


Fig. 209. Multi-unit Car for Shipping 15 One-ton Drums of Sulfur Dioxide

test, conforming to the A. S. M. E. Code. The manufacturers of sulfur dioxide are always glad to advise and assist tanners on the installation of storage tanks. The method of unloading a tank car is illustrated in Fig. 208. The storage tank is preferably located near the railroad siding. An air line with a pressure

of 50 to 70 lbs. per sq. in. is connected to a valve at the top of the car and a pipe is connected from the liquid sulfur dioxide outlet to the storage tank. This causes all the sulfur dioxide to flow from the tank car into the storage tank. The storage tank is equipped with a set of gauge cocks for measuring the amount of liquid

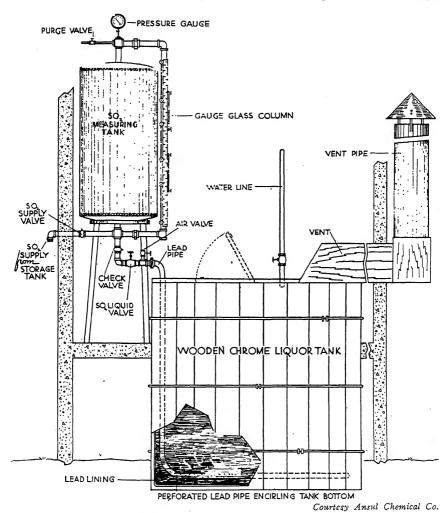


Fig. 210. Equipment for Making One-bath Chrome Liquors with Sodium Dichromate and Liquid Sulfur Dioxide.

sulfur dioxide in the tank. By opening each cock in succession from the top, the first one that spurts liquid sulfur dioxide indicates the level in the tank.

When the chrome-liquor tank is above the storage tank, the compressed-air line is used in making delivery of sulfur dioxide; when below, the sulfur dioxide can be run in by gravity.

If it is not possible to have a storage tank near a railroad siding, ton drums

may be used. Fig. 209 shows a car of 15 one-ton drums. These may be unloaded and replaced by empty drums, the car then moving back at no charge to the consumer.

The making of one-bath chrome liquor is extremely simple. A 1200-gal. mixing tank, as shown in Fig. 210, is provided with a cover with a trap door in it for adding the sodium dichromate, a vent, a water line, a lead pipe and perforated coil for introducing the liquid sulfur dioxide, and a bottom outlet. Some tanners lead-line their tanks, but this does not appear to be necessary when making chrome liquor with sulfur dioxide. Put 2000 lbs. of sodium dichromate into the tank and add water to make a total volume of 1000 gals.

Fill the measuring tank with sulfur dioxide from the storage tank and add to the dichromate solution 1290 lbs. of sulfur dioxide over a period of about two hours, at the end of which time the job is complete. As a safeguard in measuring the sulfur dioxide, tests of the liquor should be made for completeness of reduction. This is done very simply. Have on hand a bottle of 10 percent potassium iodide solution, a bottle of 1 percent potato starch solution and a bottle of 10 percent hydrochloric acid solution. Take about 4 oz. of the chrome liquor and dilute it to about one pint with water. Then add about 4 oz. of potassium iodide solution and about \(\frac{1}{2}\) oz. of the hydrochloric acid solution, mix well and add a few drops of the starch solution. If there is any unreduced dichromate left, the solution will turn a dark blue color upon addition of the starch solution. This may also be used in testing the liquors made with sugar. As long as there is any unreduced dichromate left, continue to add sulfur dioxide, but stop the addition just as soon as all the dichromate is gone. At this point, the basicity of the liquor will be exactly 33½ per cent. If sulfur dioxide is added beyond this point, the liquor will become increasingly acid and this should be avoided. After the liquor has cooled, add water, if necessary, to make the total volume exactly 1000 gals. Mix well, and the liquor is ready for use.

During the addition of the sulfur dioxide, the liquor will boil violently, but no organic acids will be formed. The writer has found liquors made in this way to be constant in composition and in tanning properties in contrast to liquors made with sugars even under the most rigid control. For many types of leathers, this liquor is quite satisfactory just as it is; but for the peculiar effects characteristic of the organic acids of sugar liquors, salts of these acids can be added as described later in this chapter.

Chrome Tanning Pickled Calfskins

We take our pickled calfskins directly after pickling, as described in Chapter 9. In order to get uniform results when basing amounts of materials to use upon pickled weight, it is necessary that the pickled stock be allowed to drain always for the same length of time and under the same conditions before weighing. The longer the draining period, the less will be the pickled weight for the same total amount of hide protein. For the procedure that follows, it will be assumed that the stock was weighed exactly one hour after pulling from the pickle and weighing as pickled weight.

Divide the stock into unit packs of 3000 lbs. pickled weight each. Put a pack into a drum 8 feet in diameter by 5 feet wide inside measurements, equipped with 8-inch pegs inside and revolving at 18 r.p.m. A battery of drums used for chrome-tanning calfskins is shown in Fig. 211. Take 50 gals of the stock sulfurdioxide chrome liquor and dilute it with water to make a total volume of 360 gals. Since each gal. of stock liquor contains the reaction products of 2 lbs, of

sodium dichromate, the 360 gals. of diluted liquor will contain the reaction products of 100 lbs. of sodium dichromate, or $3\frac{1}{3}$ lbs. per 100 lbs. pickled weight of stock. This is equal to 1.70 lbs. of chromic oxide per 100 lbs. pickled weight. Start the drum running and through the hollow gudgeon add the 360 gals. of diluted chrome liquor over a period of one hour and continue to run the drum for three hours longer. Then make cuttings of the stock and examine the cut edges of the thickest parts to make sure that the green color of the chrome has completely penetrated through the thickness of the stock. When penetration is complete, start adding very slowly a solution of 18 lbs. of soda ash in 18 gals. of water, taking a full hour to add while the drum is running. This is conveniently done by putting



Courtesy The Ohio Leather Co.

Fig. 211. Battery of Drums Used in Chrome Tanning Calfskins and Portable Frames on Which They Are Piled after Tanning.

the carbonate solution into an elevated tank equipped with an adjustable cock for regulating the rate of flow through the hollow gudgeon of the drum. Such a tank is shown to the left in Fig. 213. Continue to run the drum for another hour after all the soda ash solution has been added, and then run it for 3 min. out of each hour until next morning.

Then run the drum for 30 min. and take a sample of the liquor and a cutting of the leather. Put the cutting of leather in water and raise the temperature gradually to the boiling point, which can be done with live steam. Note the temperature at which the leather may shrink and curl. If it does not shrink or curl even in boiling water, it is well tanned and no further attention need be given to this test. Some tanners do not carry the tannage to the point that the leather will stand the boiling test and they note the temperature at which shrinking is first noticeable.

Determine the pH value of the liquor. If it is 3.0 or higher, drain off the liquor and wash the stock in running water at 70° F. for one hour. If it is less than 3.0, continue to add soda ash solution very slowly and cautiously with drum running, until the pH value is at 3.0 fifteen min. after the last addition of soda ash. Then drain off the liquor and wash the stock in running water at 70° F. for one hour. After washing, pile the stock on frames, flat trucks or wooden horses and send to be set out. Fig. 212 shows chrome-tanned calfskins being hauled from the drum and piled.



Fig. 212. Hauling Chrome-tanned Calfskins from Drum and Piling.

Although a tanner could follow the foregoing procedure and produce reasonably satisfactory leather under a rigidly controlled system, he would find that variations, according to average weight of the skins and properties of the leather desired, are necessary to get the best and most economical results.

The quantities of material and running times given were based upon the assumption that 100 lbs. pickled weight contained 20 lbs. of actual hide protein. Actually, the amount of hide protein in 100 lbs. pickled weight varies with the time and conditions of draining and upon the average thickness of the skins. Under the same conditions of draining, thicker skins contain more hide protein than thinner ones. If all skins were of exactly the same thickness and contained exactly the same amount of hide protein, a rigid procedure could be outlined that would eliminate the necessity for making tests and adjustments. However, the hide protein content of pickled stock varies widely, and no one has yet developed a

quick and simple practical method for determining the protein content of a pack of pickled stock, although the writer has made an attempt to develop such a method, which will be described later in this chapter. The most efficient operation must still be based upon experience, experiment and the careful keeping of records and study. However, an attempt will be made to show how to do this.

The procedure described above was based upon pickled stock containing 20 lbs. of hide protein per 100 lbs. of pickled weight. The pack of 3000 lbs. thus contained 600 lbs. of protein and 2400 lbs. of pickle liquor. The total amount of chrome used, calculated as chromic oxide, was 51 lbs. This is equivalent to 8.5 lbs. of chromic oxide per 100 lbs. of hide protein. By analysis, the leather contained 5.1 lbs. of chromic oxide per 100 lbs. of hide substance and the used liquor contained 0.36 gram of chomic oxide per 100 cc. This means that 60 percent of the total chrome used combined with the skins to form leather and 40 percent was run to the sewer. By greatly increasing the time of tanning and raising the pH value of the liquor slowly so as not to bring about precipitation, all the chrome can be made to combine with the skins, but the leather produced will be too soft and grainy for the best practical use. In order to improve the properties of their leather, tanners are quite willing to waste chrome liquor.

A tanner with the proper facilities can, in time, accumulate information on the average protein content of pickled stock of different average weight, for fixed conditions of pickling and draining for weighing. Although the results will only be averages, they will give him the tremendous advantage of being able to use quantities of materials based upon the average weight of protein. The adjustments to make would then be greatly minimized.



Courtesy A. F. Gallun & Sons Corp.

Fig. 213. Chrome-tan Yard Showing Testing Laboratory (right) and Feeding Tank (left).

In order to show how important it is to know the average protein content of different packs of pickled stock, let us consider an extreme case in which one pack has drained until its content of pickle liquor was only 75 percent and the other only until its content of pickle liquor was 85 percent. Taking 100 lbs. pickled weight, one would contain 25 lbs. of hide protein and the other only 15 lbs.

Basing the amount of materials to be added on pickled weight alone, one pack would receive 663 percent more material than the other per unit of hide substance. This explains why the chromic oxide contents of both leather and used liquor vary so widely in many tanneries.

In each tannery, it is a good plan to have a small testing laboratory in the chrome-tan yard, where analyses of chrome liquors can be made quickly while the stock is still in the tanning drum. Such a testing laboratory is shown to the right in Fig. 213. Methods for making such analyses are given in the book "Analysis of Leather" by Wilson and Merrill, and they can quickly be mastered by a good workman. Adjustments can then be made during the tanning to compensate for variations in protein content of packs of different average pickled weight, and the accumulated records will quickly show how much material to use for packs of different average weight.

With the addition of increasing percentages of sodium carbonate to a chrome liquor during tanning, the pH value rises. In the procedure described, when the pH value reaches some point between 3.3 and 3.6, the chrome precipitates and loses its tanning properties. By keeping the pH value just under the precipitation point, the amount of combined chrome in the leather can be greatly increased. It has the effect of making the finished leather softer and fuller, but also looser and grainier. If the final pH value of the chrome liquor is less than 2.5, the leather becomes hard, flat and tinny. Some tanners adjust the final pH value to about 2.85 in order to get very tight and smooth leather, although they make a sacrifice in softness, fulness and yield of leather. Each increase of 0.1 in pH value makes the leather softer, fuller and of greater yield, but it also makes it looser, rougher and of coarser break.

For stock that is naturally of denser and tighter structure, the pH value can be raised higher to actual advantage. In any single skin, the tight butt area can be improved by raising the pH value above 3.0, but the flanks suffer by becoming so loose as to lose their cutting values.

The best procedure to follow in the chrome-tan yard depends both upon the subsequent operations and upon the particular properties desired in the finished leather. Judgment on this must be made by the tanner himself. The procedure outlined will form a good starting point for any tanner, and it is hoped that the remarks following it will prove a sufficient guide for the tanner to make adjustments in details to his best advantage.

Fig. 214 shows a cross-section of chrome-tanned calfskin. The skin before tanning was cut into sides along the line of the backbone and one side was vegetable-tanned and the other chrome-tanned. A cross-section of the vegetable-tanned side is shown in Fig. 173 of Chapter 11. Chrome-tanning does not build up the fibers to the same extent as vegetable tanning.

Determination of Hide-substance Content of Pickled Stock Before Chrome Tanning

It was pointed out above how very valuable it would be to know the actual weight of hide substance in a pack of pickled stock to be chrome-tanned. Then the amounts of materials to use in tanning could be based upon the actual hide substance and not upon a variable pickled weight. The writer has developed a method for determining the amount of hide substance in a given pack that he has used successfully on a few packs of light skins, but which requires too great a precision of analysis for routine work. A description of the method is in order because it may lead to the development of a precision method of analysis com-

parable with that of the determination of pH value with the glass electrode, which hardly a decade ago seemed too complex for general use.

In this method, it is merely necessary to make accurate determinations of the chlorides in pickle liquors. In many tanneries, this determination is run as a matter of routine, but not with the accuracy required for calculations of hide substance. In calculating the hide-substance content of a pack, the chlorides are

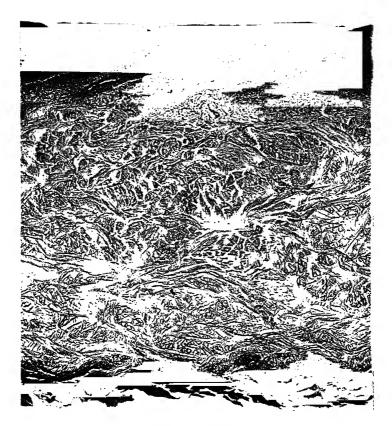


Fig. 214. Vertical Section of Chrome-tanned Calf Leather.

Location: butt.

Thickness of section: 40 microns, or 0.00158 inch.

Magnification: 75 diameters.

first determined in the used pickle liquor from which the pack to be tanned has been taken. In a test which we shall use for an illustration, this was found to be 11.95 lbs. per 100 lbs. of pickle liquor, calculated as sodium chloride. The pack of 3000 lbs. pickled weight was then put into the tanning drum, covered with 2000 lbs. of water (240 gals.) and run for 2 hours. Then the chlorides were determined in the diluted pickle liquor from the drum and found to be 6.56 lbs. per 100 lbs. of diluted pickle liquor, calculated as sodium chloride. The original 3000 lbs. of pickled weight contained the unknown amount, x lbs., of hide substance and

(3000 - x) lbs. of pickle liquor; but the pickle liquor contained 11.95 percent by weight of chloride, calculated as sodium chloride, and so the pack contained a total of 0.1195 times (3000 - x) lbs. In the tanning drum, after diluting with 2000 lbs. of water and running to equilibrium, there is still x lbs. of hide substance and the same total amount of chlorides that was present in the original pack, but there is now (5000-x) lbs. of diluted pickle liquor containing 6.56 percent by weight of chlorides, calculated as sodium chloride. The total number of lbs. of chlorides in the drum is thus 0.0656 times (5000 - x), but this we know to be equal to 0.1195 times (3000 - x) lbs. From this, it is a simple algebraic problem to calculate the value of x as 566, the number of lbs. of hide substance in the pack. After this calculation was made, the true hide-substance of the entire pack was determined after the tanning by a very elaborate and costly method and found to be 564 lbs., showing that the method is reliable, if the chlorides can be determined with sufficient accuracy. The chloride determination must be accurate to the second decimal place or the calculation of hide substance will not be accurate enough for safe use. In the average well-run tannery, accuracies in this determination within the second decimal place are not to be expected; therefore the method should not be attempted until this accuracy can be guaranteed. The calculation can also be made from the decrease in specific gravity of the pickle liquor upon dilution, but here the determination of specific gravity must be accurate to 0.0001.

To continue with the procedure after calculating the amount of hide substance to be 566 lbs.: Each 100 lbs. of hide substance requires 8.5 lbs. of chromic oxide in 60 gals. of liquor. The pack has already received 240 gals. of water. It needs a total of 48.1 lbs. of chromic oxide, which is contained in 47.2 gals. of stock chrome liquor. It requires a total volume of diluted chrome liquor of 339.6 gals., and so the 47.2 gals. of stock chrome liquor is diluted with water to make 99.6 gals. and added to the drum. After that, proceed as described above.

Chrome Tanning Pickled Cowhides

The chrome-tanning of heavy hides does not differ in principle from the chrome-tanning of light skins. Although the thickness of the hides makes a great deal of difference in vegetable tanning, it makes very much less difference in chrome-tanning because the chrome penetrates the hides very much more rapidly than do the vegetable tannins. However, the thickness of the hides markedly affects the properties of the leather, and it is often desired to impart to cowhide leather properties different from those of calf leather.

After pickling, a pack of 3000 lbs. of cowhides contains less water than a pack of 3000 lbs. of calfskins, under the same conditions of draining. For this reason it contains more hide substance. As a rule, the hide-substance content of a pack of 3000 lbs. pickled weight increases with the average weight of the hide or skin. It has thus become customary for a tanner to use increasing quantities of material per unit of pickled weight as the average weight of hides or skins increases. His formulas usually include tables showing the amounts of different materials to use per unit of pickled weight based upon average weight. The properties desired in heavier leathers often call for a greater fixation of chrome, and this requires substantially more chrome per unit of pickled weight than is required for calfskins.

In making shoe-upper leather from cowhides, it is customary to split the leather after tanning so that the grain side has a thickness suitable for shoe uppers. The flesh side is then converted into special leathers, known as splits. Before pickling and chrome tanning, cowhides are usually cut into sides for convenience in handling.

Follow the procedure outlined for calfskins, but increase quantities of materials according to average pickled weight. For 3000 lbs. of 40-lb. cowhides for shoe-upper leather, use 60 gals. of the stock chrome liquor diluted to make a total volume of 432 gals. Follow the penetration of the chrome through the thickness of the hides and do not add sodium carbonate solution until the stock has been completely penetrated by chrome. It may require about 21 lbs. of soda ash to bring the pH value of the liquor to 3.0 by the next morning. This should be added in 21 gals. of water very slowly over a period of one hour. The drum should be run continuously from the time the pickled stock enters it until one hour after all the soda ash solution has been added and then for 3 min. each hour until next morning. The stock should then stand the boiling test. If the pH value of the liquor is below 3.0, enough more soda ash should be added to raise it to 3.0. Then haul out the stock and pile it.

Although calfskins are often washed immediately after tanning, it is customary not to wash stock to be split until after the splitting operation. The stock is allowed to lie in piles over night and is then set out under heavy pressure and sent to the splitting room.

Sometimes it is desired to make chrome-tanned cowhide leather that is very full and mellow, and sometimes it is required to make leather that will resist the action of steam under pressure. Both results can be accomplished by increasing the amount of chrome fixed per unit of hide substance several fold. This can be done by increasing the amount of stock liquor used per unit of pickled weight, extending the time of tanning and, after the stock has been completely penetrated by chrome, maintaining the pH value of the liquor just under but never exceeding that at which the chrome precipitates.

In making this type of leather, it is important to make precipitation tests before each addition of soda ash to the chrome liquor so that as much as possible may be added without causing any precipitation of the chrome. In this test, invented by McCandlish, a standard solution is used containing 12 grams of soda ash per liter. A burette graduated in tenths of a cc. is filled with this solution. Take a sample of chrome liquor from the drum and filter it so that a transparent filtrate is obtained. Pipette 10 cc. of the filtrate into a 25-cc. beaker. Hold the beaker over a watch face so that the face can be seen clearly through the transparent green liquor. Then add to the liquor, drop by drop, the standard solution from the burette, shaking after each addition and then looking through the liquor at the watch face. A point will finally be reached where the liquor clouds because of precipitation of the chrome and the watch face can no longer be seen through the liquor. This represents the precipitation point. Note from the burette reading how many cc. of the standard solution were required to bring about precipitation in 10 cc. of chrome liquor. This reading represents the number of pounds of soda ash that may safely be added per 100 gals, of chrome liquor in the drum, without causing precipitation.

This amount of soda ash will not start precipitation in the drum because the water carried into the drum by the pickled stock forms a part of the total volume of liquor in the drum, and it is not taken into consideration in making the calculation for amount of soda ash to add. In other words, the amount of soda ash added is just enough to start precipitation in the volume of liquor added to the drum, but not enough to start precipitation in the total volume of liquor that is in the drum including that carried in by the pickled stock.

Put a pack of 3000 lbs. pickled weight of stock into the drum and add 180 gals. of the stock chrome liquor diluted with water to make a total volume of 500 gals. After running the drum until the stock has been completely penetrated by the

chrome, take a sample of the liquor and determine the precipitation value. Add the amount of soda ash called for, using 1 gal. of water per lb. of soda ash, slowly over a period of one hour. For example, if it required 6.1 cc. of standard solution to start precipitation in 10 cc. of the chrome liquor, add 6.1 lbs. of soda ash per 100 gals. of liquor in the drum, or a total of 30.5 lbs. of soda ash in 30.5 gals. of water. Keep the drum running continuously, and 4 hours after the last addition of soda ash, again determine the precipitation value and again add soda ash accordingly. Run the drum for at least one hour after the last addition of soda ash and for 3 min. each hour during the night. Next morning again make a precipitation test and again add soda ash accordingly. This can be repeated until the chrome liquor is nearly exhausted, although the tanning time may run as long as 3 days.

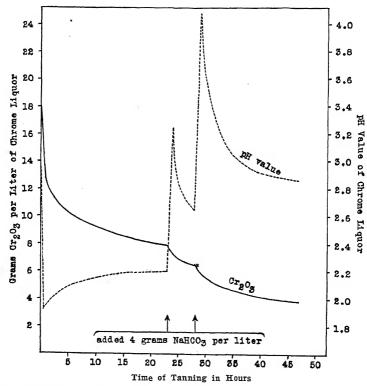


Fig. 215. Changing pH Value and Chromic Oxide Content of Chrome Liquor During the Tanning of Cowhides.

In the calf process described, the number of lbs. of chromic oxide fixed by 100 lbs. of hide substance may vary from 3 to 6 lbs., depending upon the tanning time and point to which the pH value is raised, but in this process, the amount fixed will vary from 12 to 14 lbs. The leather will be very full, soft and mellow, and it will resist the action of steam up to about 300° F. Taking this process and the calt process as extremes, a whole series of processes can be developed, changing gradually from one to the other. In this way, the best process for any desired properties of the leather can readily be determined.

Fig. 215 shows the changing composition of a chrome liquor used to tan cowhides by a procedure intermediate between the two extremes described. The pack of 3000 lbs. pickled weight was given the equivalent of 120 gals. of stock chrome liquor in a total volume of 450 gals. and was not neutralized until the following day, when the pH value was 2.20. The liquor was then treated with 15 lbs. of sodium bicarbonate in 20 gals. of water, added over a period of one hour, and then the drum was run for 4 hours after the last addition of bicarbonate. Then the same amount of bicarbonate was added again and the stock remained in the drum until the following day. Formerly sodium bicarbonate was commonly used as the neutralizing agent, but now soda ash is more commonly used because it gives exactly the same result and is less expensive and bulky; 1 lb. of soda ash has the same neutralizing power as 1.58 lbs. of sodium bicarbonate.

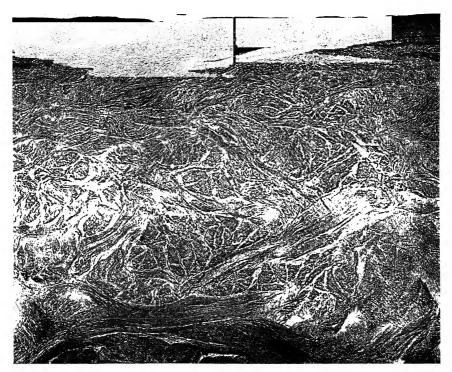


Fig. 216. Vertical Section of Chrome-tanned Cowhide Leather.

Location: butt.

Thickness of section: 30 microns, or 0.00118 inch.

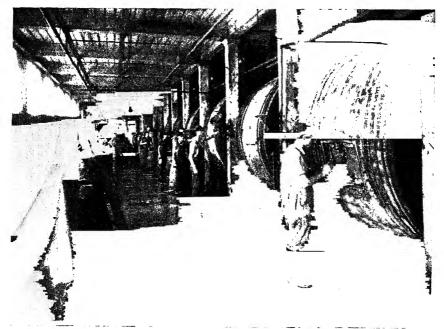
Magnification: 67 diameters.

120 grams of Cr_2O_3 per liter means the same as 1 lb. of chromic oxide per gal. and 4 grams of NaHCO₃ per liter means the same as $3\frac{1}{2}$ lbs. of sodium bicarbonate per 100 gals.

During the first half-hour of tanning, the pH value of the liquor drops rapidly because the acid from the pickled skin diffuses into it. Then the pH value of the liquor rises. It is characteristic of chrome liquors that changing their pH values

in either direction is always followed by a slow recovery toward the initial pH values. There is a sharp rise in pH value upon the addition of bicarbonate, followed by a drop with time. The second addition of bicarbonate raises the pH value above 4.0, and this is followed by a drop. If all the bicarbonate had been added at once, the chrome would have precipitated and the stock would have become very grainy and discolored. With successive determinations of precipitation value and additions only of the amounts of bicarbonate or soda ash called for, the chrome liquor can be exhausted and the pH value raised above 6.0 with no precipitation of the chrome, all of it combining directly with the hide protein to form leather.

Fig. 216 shows a cross-section of a typical chrome-tanned cowhide which was split for shoe-upper leather. Fig. 217 shows a battery of drums used for chrome tanning cowhides. At the left of this picture can be seen the tank used for storing the stock chrome liquor.



Courtesy of Bona Allen, Inc.

Fig. 217. Showing Battery of Drums Used in Chrome Tanning Cowhides.

Chrome Tanning Goatskins by Two-bath Process

In the two-bath process, the sodium dichromate is not reduced to chromic sulfate until after it has penetrated through the stock, and it does not combine with the hide protein in such manner as to form satisfactory leather until after it has been reduced. In some procedures, the bated skins are first treated in a paddle vat with a solution of sodium dichromate, and then in another paddle vat with a solution of hypo.

One process in use is as follows: Into a paddle vat of 2500-gals. capacity, put 240 lbs. of sodium dichromate dissolved in 2100 gals. of water and add 86 lbs. of 66° Baumé sulfuric acid. Mix well and dump a pack of 3000 lbs. bated weight

of goatskins into it. The stock is taken directly from the bate, after scudding and washing. Run the paddle for 2 hours and then take a sample for analysis of its acid content. If the stock has not been thoroughly delimed, a certain amount of the acid will be neutralized by the lime in the stock, and this must be replaced.

Filter the sample and pipette 25 cc. of the filtrate into an Erlenmeyer flask. Add a few drops of phenolphthalein solution and titrate by adding standard tenthnormal sodium hydroxide from a burette until the color of the solution changes first from orange red to yellow and then to an orange pink shade, which is a mixture of the yellow color of the chromate and the violet red of alkaline phenolphthalein. Note exactly the number of cc. of the standard solution required and subtract this number from 39.7. Multiply the difference by $4\frac{1}{3}$; this gives the number of lbs. of 66° Baumé sulfuric acid to add to the paddle vat. For example, if the number of cc. of standard solution required to neutralize the acid in 25 cc. of the sample was 30.7, by subtracting this from 39.7 we would get 9.0; multiplying 9.0 by $4\frac{1}{3}$, we would get 39, the number of lbs. of acid to add to the liquor in the paddle vat. In adding this acid to the liquor, first take out a barrel of the liquor, add the acid to it, mix well and then pour the liquor back into the vat with the paddle running. Run the paddle for an hour after adding the acid and then allow it to stand over night. Next morning run the paddle for 30 min, and haul out the stock, pile it on wooden horses and allow it to drain for an hour. Then set out the skins to make each skin smooth and then put them one by one into the second bath.

The second bath is made up in a paddle vat of 2500-gals. capacity by filling it with 300 lbs. of hypo dissolved in 2100 gals. of water. Immediately before putting the skins into this vat, start the paddle running and add 85 lbs. of 66° Baumé sulfuric acid. Then put all the skins in with the paddle running and continue to run the paddle for 3 hours, and for 5 minutes out of each hour until next day. Then haul out the stock, put it into a drum, and wash in running water at 70° F. for one hour. Then send it to be set out and shaved.

The first bath contained about twice as much sodium dichromate as the skins required; it can be used for about 7 successive packs by analyzing it after each use for sodium dichromate and total acid and adding enough sodium dichromate and sulfuric acid to restore its composition each time to the same as it was before the first pack entered it. Whenever a tanner uses the same liquor for successive packs of skins, he should have analyses made to insure against varying composition of the liquors. The initial pH value of the first bath will be about 1.6, but this is not controlled. It is desirable, however, that the pH value of the used second bath should be controlled at about 3.3.

Many goatskin tanners prefer to use 20° Baumé muriatic acid instead of sulfuric acid as it produces a leather of slightly different characteristics. In order to use muriatic acid in the above procedure, simply use 2.2 lbs. of 20° Baumé muriatic acid in place of each lb. of 66° Baumé sulfuric acid.

A number of tanners carry on the two-bath process in a single drum. One procedure is as follows: Put a pack of 3000 lbs. bated weight into the drum, start running and add 120 lbs. of sodium dichromate and 73 lbs. of sulfuric acid dissolved in water to make 300 gals. at 70° F. Run drum for 1 hour and then add 85 lbs. of 66° Baumé sulfuric acid in 50 gals. of water at 70° F., followed immediately by 300 lbs. of hypo dissolved in 150 gals. of water at 70° F. Run drum for 3 hours longer and then measure the pH value of the liquor. If it is less than 3.3, add enough soda-ash solution over a period of 1 hour to raise it to 3.3, run 1 hour longer and then dump the pack, pile it on wooden horses and send to be set out and shaved.

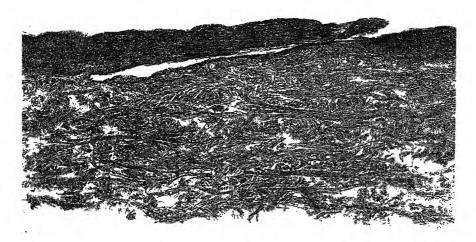


Fig. 218. Vertical Section of Goatskin Leather Tanned by One-bath Process with Liquor Made by Reducing Sodium Dichromate with Sulfur Dioxide.

Location: butt.

Thickness of section: 30 microns, or 0.00118 inch. Magnification: 64 diameters.

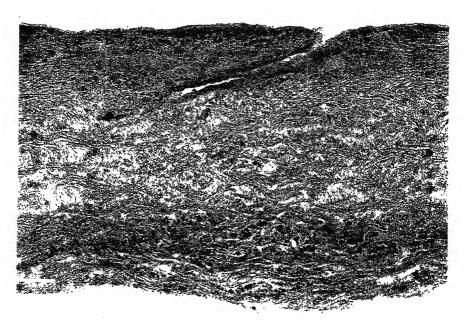


Fig. 219. Vertical Section of Goatskin Leather Tanned by Two-bath Process.

Location: butt.
Thickness of section: 30 microns, or 0.00118 inch.
Magnification: 64 diameters.

In regulating the final pH value of the liquor, it should be noted that at pH = 2.9 the leather will be very smooth, but somewhat hard and flat; as the pH value is raised to about 3.6, the finished leather becomes softer and fuller, but rougher. Individual tanners adjust the pH value according to the properties desired in the leather, and according to details of the procedures to follow.

Some tanners use the syntan *Leukanol* after the hypo, and may add as much as 120 lbs. diluted to 60 gals. with water one-half hour after the last addition of hypo. This has the effect of increasing the fulness of the leather without the necessity of raising the pH value to the point where the leather becomes rough.

Goatskins also are often tanned by the one-bath process, pickling after bating, as described in Chapter 9, and following the procedure given for calfskins. For a pack of 3000 lbs. pickled weight, it is customary to use 60 gals. of stock chrome liquor (containing the reaction products of 2 lbs. of sodium dichromate per gal.) The final pH value is brought to about 3.2.



Fig. 220. Vertical Section of Boxing-glove Leather (Chrome-tanned Sheepskin).

Location: butt.

Thickness of section: 30 microns, or 0.00118 inch.

Magnification: 32 diameters.

Fig. 218 shows a cross-section of a typical goatskin tanned by this one-bath process and Fig. 219 a goatskin tanned by the two-bath process described, in which Leukanol was added after the hypo. The appearance of the fibers is noticeably different in the two leathers, and the feel and general characteristics were correspondingly different. This is not so much because one was made by the one-bath and the other by the two-bath process, as because of the difference in chemical composition of the complex chromium salts that combine with the hide protein. When the one-bath chromic liquor is made by reducing the sodium dichromate with hypo, the leather produced is much more nearly like the two-bath leather. Leukanol can be

used with either the one-bath or two-bath process, with much the same effect. When using hypo, free sulfur is liberated in very finely divided form, and the presence of this sulfur in the leather has a slight effect upon its properties.

Chrome Tanning Sheepskins by One-bath Process

A number of tanners chrome tan sheepskins for manufacture into leather for garments, boxing gloves, etc. They usually add aluminum sulfate to the chrome liquor before tanning because it appears to make the leather somewhat tighter, smoother and fuller. Many tanners of other types of leathers also use aluminum sulfate in the same way. A typical procedure for sheepskins is as follows: Put a pack of 3000 lbs. of pickled sheepskins, after degreasing, into a drum, start it running, and add 150 lbs. of aluminum sulfate and 60 gals. of stock chrome liquor dissolved in water to make 300 gals, at 80° F. Run one hour and then add slowly, over a period of one hour, 30 lbs. of soda ash in 30 gals. of water. Run for one hour after all the soda-ash solution has been added and then measure the pH value of the liquor. If it is below 3.4, add enough more soda-ash solution to raise it to 3.4, taking one hour to add, run the drum for another hour and then dump and pile the stock and let it remain piled over night. Then send to be shaved. Fig. 220 shows a cross-section of a typical sheepskin tanned by this process for boxing-glove leather. Fig. 221 shows a department for chrome tanning both sheepskins and goatskins.

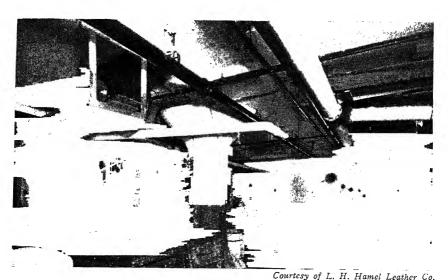


Fig. 221. Department of Tannery for Chrome Tanning Both Sheepskins and Goatskins.

Chrome Tanning Sole Leather

Nearly all sole leather is vegetable-tanned; some, however, is chrome-tanned for special use. Chrome-tanned sole leather has the disadvantage of becoming slippery when wet, unless it is specially treated, and does not give the yields of leather desired unless it is heavily loaded with greases or other materials. On the other hand, it has a resistance to abrasion and wear about three times as great as that of vegetable-tanned sole leather. It can also be made much more quickly. It has

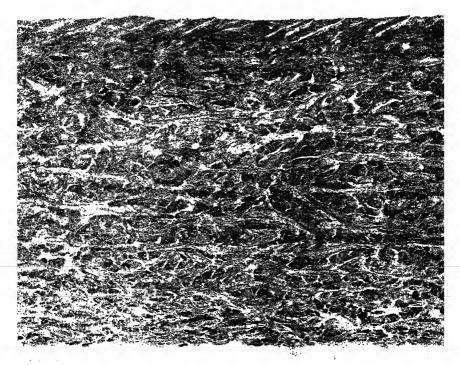


Fig. 222. Vertical Section of Chrome-tanned Sole Leather from Shoulder of Steer Hide.

Location: shoulder.

Thickness of section: 40 microns, or 0.00158 inch.

Magnification: 14 diameters.

the further advantage for special purposes of being much more resistant to heat than vegetable-tanned leather. It is unaffected by boiling water, whereas vegetable-tanned leather is damaged by contact with water much above 150° F. For the best and heaviest types, the butts of steer hides are used, but for boys' shoes shoulders and sometimes even bellies are used to keep the cost down.

The procedure is essentially the same as for calfskins, except for the use of a greater amount of chrome based on pickled weight and the increase in tanning time. Care must be taken not to add the soda-ash solution until after the stock has been completely penetrated by the chrome. Excessive drumming is avoided to prevent the stock from breaking up and becoming loose. Usually soda-ash solution is not added until after the stock has been in the liquor over night. For heavy butts, neutralization with soda ash is apt to be a slow procedure because of the long time required for the soda ash to penetrate through the thickness of the hides. It is desirable, therefore, to use the precipitation test together with the pH value while neutralizing to avoid any precipitation, which would discolor the stock and make it grainy. About twice as much chrome liquor should be used on heavy stock as for calf, and the tanning time may have to be extended to as long as 3 days. The final equilibrium pH value should be about 2.9. Light shoulders can easily be tanned in one day.

Some tanners do the tanning in paddle vats to avoid making the stock loose by excessive drumming and to conserve chrome liquor, but this greatly extends the tanning time and necessitates the reuse of liquors. In making up a used liquor for a new pack of pickled stock, it is easy to bring the chrome content and the pH to their initial values; but with each successive use, there is an increase in the salt content due to the salt brought in by the pickled stock and the salt formed by neutralization, as well as to the salt present in the chrome liquor. With increasing concentration of salts, there is a decreasing fixation of chrome by the hide substance. However, some tanners add enough salt to a fresh liquor so that each pack carries out of the liquor as much salt as that by which the salt content of the liquor is increased by each pack. They then adjust the final pH value to a higher level in order to get a greater fixation of chrome. When using the paddle vat. each liquor after using should be analyzed for chromic oxide, total acid, sulfates, chlorides and pH value, so that the liquor can be made up for the next pack to match the standard composition adopted. The methods for these analyses can be found in the book "Analyses of Leather," by Wilson and Merrill.

The pack should not be taken from drum or paddle vat until it can stand the boiling test; that is, a strip of the leather kept in boiling water for 5 minutes should not shrink or curl. After the stock is tanned, it should be piled for 2 days and then set out and sent ahead for the subsequent operations.

Fig. 222 shows a cross-section of chrome-tanned sole leather made from the shoulder of a steer hide. This type of leather is used for boys' shoes.

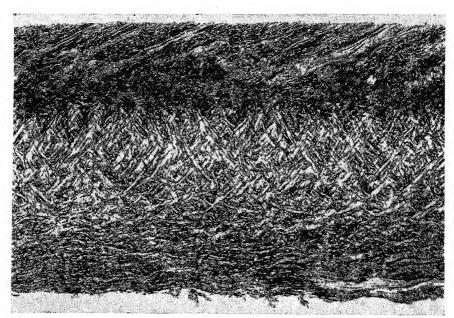


Fig. 223. Vertical Section of Chrome-tanned Horse Butt (Shell Cordovan).

Location: butt.

Thickness of section: 30 microns, or 0.00118 inch.

Magnification: 32 diameters.

Chrome Tanning Horsehides

In tanning horsehides, the fronts are usually tanned separately from the butts because of their great differences in density and structure. The fronts, being of loose structure, are made into leather for garments, workmen's gloves, etc. The butts, being very dense, are often made into the leather for hard use known as shell cordovan.

In tanning the butts, the procedure is essentially the same as for chrome-tanned sole leather. For the fronts, it is essentially the same as for cowhides.

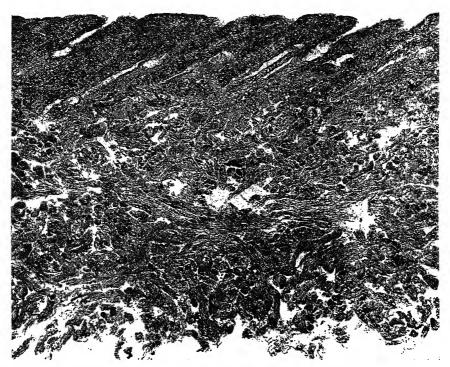


Fig. 224. Vertical Section of Chrome-tanned Horse Front (Glove Leather).

Location: shoulder.

Thickness of section: 30 microns, or 0.00118 inch.

Magnification: 29 diameters.

Fig. 223 shows a cross-section of chrome-tanned horse butt, known as shell cordovan, for heavy shoe-upper leather, and Fig. 224 a cross-section of chrome-tanned horse front for workmen's gloves. The looseness of structure of the horse front stands out in marked contrast to the dense structure of the shell of the butt.

Chrome Tanning Shearlings

Sheepskins and lambskins tanned with the wool on are widely used for cheap fur coats and other fur garments. The best raw stock is imported as dry shearlings, but some green, salted stock is used. Before tanning, the dry skins are first soaked for 2 days in fresh water at about 50° F., the water after 1 day being replaced by fresh water. Green, salted skins are not given this preliminary soaking, but both types are treated the same after the soaking of the dried skins.

Tanners of unhaired hides and skins usually use either the bated weight or the pickled weight as a basis for determining the amounts of materials to use in tanning. These weights are so variable in relation to true hide substance, which is the scientific basis for determining the required quantities of materials, as to cause much trouble and variation even when carefully controlled. In the case of sheepskins with the wool on, the amount of water carried by them under any set conditions varies greatly with the length and nature of the wool and with many other factors. For this reason, it is customary for the shearling tanner to base amounts of materials to use upon numbers of skins of a given type. He divides the incoming skins into packs of different average weight and kind, according to his recorded previous experience.

For an average lot of 75 skins, either dry skins that have been soaked 2 days or green, salted skins as received, proceed as follows: First trim the lot and then put into drum and wash in running water at 80° F. for 10 min. and drain. Dissolve 12 lbs. of soda ash and 9 lbs. of oleate soap in 15 gals. of water at 100° F., add 3 gals. of naptha, mix well and add to the drum while running. Run for 15 min. and then dump and pile the skins. Then flesh the skins and examine the wool for card marks. Remove these card brand marks by rubbing them thoroughly by hand with soap solution made by dissolving 8 oz. of oleate soap in 1 gal. of water. After rubbing the marks thoroughly with soap solution, let stand for 10 min. and rinse with cold water.

Then put the lot of skins back into the drum for the second degreasing. Add 15 lbs. of oleate soap and 6 lbs. of soda ash dissolved in 18 gals. of water at 100° F., run 15 min. and drain. Wash the stock in running water at 85° F. for 10 min. and drain. Then wash in running water at 60° F. for 5 min., haul out the stock, pile on wooden horses and let stand for 2) hours to drain. Assort according to average weight, length of wool, damage, etc. into packs of about 500 average skins and send to be tanned.

In chrome tanning skins with the wool on, it is important to minimize, as far as possible, combination of chrome with the wool, which may seriously impair the appearance of the wool after dyeing. For this reason, the methods of chrome tanning found best for unhaired skins cannot be used.

Into a paddle vat of 2500-gals. capacity, put 1250 lbs. of salt and enough water at 70° F. so that the addition of the 500 skins will just fill the vat to the 2300-gal. mark. Make sure that all the salt is dissolved and then dump in the skins. Run the paddle for 5 min. and then add slowly 40 lbs. of 66° Baumé sulfuric acid in 40 gals. of water. After all the acid is in, run for 30 min, and add 40 lbs. of aluminum sulfate in 40 gals. of water. Run 30 min. longer and let stand over night. Next morning run the paddle for 5 min. and then add 40 lbs. of aluminum sulfate in 40 gals. of water and run for 30 min. Let stand for 3 hours and add 80 lbs. of chrome alum in 50 gals. of water, run for 1 hour and let stand over night. Next morning, run paddle for 15 min. and then add 6 lbs. of soda ash in 6 gals. of water over a period of 45 min., run for 30 min. longer and let stand for 3 hours. Then run for 5 min. and determine the pH value of the liquor. If it is above 3.2, add no more soda ash; if below 3.2, add just enough more sodaash solution to bring the pH value to 3.2. It is desirable to control the addition of soda ash with both the precipitation test and pH value. Never add soda-ash solution in such quantity or at such speed as to raise the pH value above 3.2, or to

start precipitation of chrome. Always run the paddle for 20 min. after any addition of soda ash. When the pH value has been brought to 3.2, let stand over night.

Next morning, bring the pH value to an equilibrium pH value of 3.2, haul out the stock and send it to be wrung out. The subsequent operations will be described in Chapter 17. Fig. 225 shows a cross-section of chrome-tanned shearling taken after finishing.

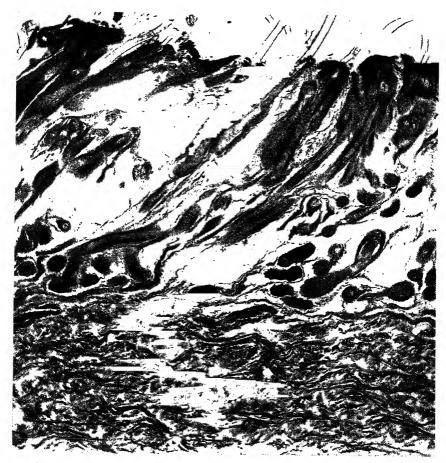


Fig. 225. Vertical Section of Chrome-tanned Shearling.

Location: butt.

Thickness of section: 30 microns, or 0 00118 inch.

Magnification: 75 diameters.

Commercial One-bath Chrome-tanning Materials

After the development of one-bath chrome tanning by Martin Dennis, manufacturers were quick to place on the market prepared materials ready for use, such as *Tanolin* by The Martin Dennis Company and *Koreon* by Röhm & Haas Company. These materials are prepared both as solids and as liquids and of dif-

ferent compositions for special uses, letters being placed after their names to indicate the composition and use. Many tanners prepare their own one-bath liquors to effect an economy, but others believe that the premium charged is a small price to pay for having their materials manufactured by specialists. The methods for making one-bath chrome liquors, both with sugars and with sulfur dioxide, were described above to help a tanner to make his own where he found it to his advantage. In the procedures described above, the sulfur dioxide liquor was taken as the standard, because it is easier to make it of constant composition than the sugar liquors, which differ greatly in composition and in properties when made in different ways. Manufacturers of one-bath chrome-tanning materials sometimes use both sugars and sulfur dioxide, and sometimes add aluminum sulfate and other substances to impart special properties to the tanning materials. Details of their methods of manufacture are kept secret to safeguard them against competition.

Chrome Tanning for White Leathers

Vegetable-tanning and chrome-tanning comprise the two major tannages, but both impart color to the hides and skins—the former various shades of tan and the latter shades from green to blue. White leathers are often tanned with substances which impart no color to the hides and skins, such as aluminum sulfate, formaldehyde, Leukanol, sodium tungstate, Calgon, etc., which will be described in Chapter 13. In order to give white leathers some of the desirable properties resulting from chrome-tanning, some tanners include chrome-tanning in the procedure and then lessen or mask the color in various ways. In chrome-tanning, the less chrome fixed by the hide substance and the greater the acidity of the chromium complex in the leather, the lighter is the color produced in the leather. When the color is made a very light blue, it is easy to mask it by the use of inert white pigments.

An old method was to follow the procedure given above for calfskins, except that the amount of chrome liquor was cut in half, and one-half pound of salt per gallon of chrome liquor was added, raising the pH value only to 2.8. The stock then would not stand the boiling tests. It was set out, split and shaved and returned to the tanning drum. The procedure for a pack of 1000 lbs. shaved weight (about 500 lbs. dry weight) is as follows: Put pack into drum and wash in running water at 70° F. for one hour. Drain and add 120 gals. of water at 90° F. Run and start adding slowly 50 lbs. of hypo dissolved in 50 gals. of water at 90° F., taking one hour to add. Run 30 min. longer and add 50 lbs. of Leukanol in 25 gals. of water at 90° F. Then run for one hour and drain. Wash in running water at 90° F. for 15 min. and drain. Add 30 lbs. of barium chloride in 60 gals. of water at 90° F., run 1 hour, pile on truck and let stand over night.

Next day put pack back into drum, add 30 lbs. of anhydrous Glauber's salt in 120 gals. of water at 70° F., run for 1 hour and drain. Wash in running water at 140° F. for 10 min. and drain. Add 80 lbs. of Titanox A (titanium dioxide) stirred up with 80 gals. water at 140° F. and run 5 min. Then add 50 lbs. of sulfonated coconut oil in 120 gals. of water at 140° F. Run 30 min., dump the pack, pile on trucks and let stand over night. Next day set out the stock as smoothly as possible, apply a coat of white pigment finish to the grain, as described in Chapter 17, and send to be dried.

In the following procedures for chrome-tanning stock for white leathers, the tanning material is a commercial product known as Tanolin-W2XD and manufactured by Martin Dennis Company. A stock liquor is prepared by adding 1000 lbs. of Tanolin-W2XD to boiling water, in sufficient quantity to make 300 gals. of

liquor after cooling. After adding the Tanolin-W2XD to the boiling water, the liquor should be boiled for 5 min. and allowed to cool to 85° F.

Chrome Tanning Cowhides for White Leathers

Take the stock after pickling, as described in Chapter 9. Put a pack of 1000 lbs. pickled weight into the tanning drum and add 60 lbs. of salt in 50 gals. of water at 85° F. and run 10 min. To 30 gals. of the stock Tanolin-W2XD liquor add 20 lbs. of formaldehyde and adjust the temperature to 85° F. Add one-third of this liquor to the drum and run 30 min. Add the second third and run 60 min.; then add the last third and run 90 min. Then dissolve 6 lbs. of soda ash in 30 gals. of water, add 10 gals. to the drum at once, and run 45 min.; add the second 10 gals. and run 60 min., and then add the last 10 gals. and run 60 min. The stock should then stand the boiling test, but, if it does not, add more soda ash solution cautiously until it does. Then drain and wash the stock in running water at 70° F. for 10 min. Then horse the stock and let stand over night.

Next day set out, split and shave and return to drum. Put a pack of 1000 lbs. shaved weight into drum and add 50 lbs. of flour and 50 lbs. of Ti-Pure-LW (Martin Dennis Co.) in 20 gals. of water at 120° F. Run 15 min. and add 27½ lbs. of Acidolene-243 in 80 gals. of water at 130° F. Run 30 min., dump and pile on horses and let stand over night. Next day, set out and hang to dry.

Chrome Tanning Goatskins for White Leathers

Take the stock after pickling, as described in Chapter 9. Put a pack of 1000 lbs. pickled weight into the tanning drum and add dry 50 lbs. of salt and 50 lbs. of crystalline Glauber's salt and run 15 min. Then add dry 60 lbs. of flour and 50 lbs. of Colloidal Clay-A (Saxe-Rushworth Co.) and run 10 min.

To 30 gals. of the Tanolin-W2XD stock liquor add 10 lbs. of formaldehyde and dilute with water to make 40 gals. at 100° F. Add one-half of this liquor and run 30 min. and then the other half and run 90 min. Dissolve 6 lbs. of soda ash in 40 gals. of water at 85° F. Add 20 gals. and run 15 min., and then the remaining 20 gals.; run 45 min. and drain. Wash in running water at 85° F. for 45 min., horse the stock and let stand over night. Next day, set out, shave and weigh as shaved weight.

Put pack of 1000 lbs. shaved weight into drum and wash in running water at 85° F. for 15 min. and drain for 15 min. Mix 20 lbs. of Tanagan-DLN (General Dyestuff Corp.) with 50 gals. of water at 145° F., add to drum and run for 30 min. Drain and wash in running water at 100° F. for 10 min. and then drain for 15 min. Add 240 gals. of water at 125° F. and run for 1 min. Add 60 lbs, of Acidolene-283 (Martin Dennis Co.) in 30 gals. of water at 125° F., run 20 min. and add 30 lbs. of Ti-Pure-LW (Martin Dennis Co.) mixed with 30 gals. of water at 125° F. and run for 20 min. Horse the stock and let stand over night. Next day set out on flesh side, hang to sammy and then tack or toggle on frames to dry.

Chrome Tanning Pickled Sheepskins for White Leathers

Take pickled stock after degreasing and put 1000 lbs. of original pickled weight of stock into the tanning drum. Add 90 lbs. of salt and 2.5 lbs. of 66° Baumé sulfuric acid in 90 gals. of water at 80° F. and run 30 min. Add 15 gals. of stock Tanolin-W2XD liquor as 80° F. and run 30 min. Then add 15 gals. of stock Tanolin-W2XD liquor at 80° F. and run 90 min. Dissolve 9 lbs. of soda ash in 30 gals. of water at 85° F. Add 10 gals. of this solution and run 30 min. Then add the second 10 gals. and run 30 min. Add the last 10 gals. and run 60 min. If

stock then will not stand the boiling test, add more soda-ash solution cautiously until it will. Drain and wash with running water at 70° F. for 5 min. and then haul out and flesh.

Put back into drum and wash in running water for 15 min. at 70° F. and then for 15 min. at 120° F., and drain. Add 30 lbs. of titanium dioxide and 100 lbs. of flour mixed with 20 gals. of water at 120° F., and then 30 lbs. of Acidolene-209 (Martin Dennis Co.) in 80 gals. of water at 125° F. Run 30 min. and horse the stock. Let stand over night and then set out and hang to dry.

Chrome Tanning Sheepskin Skivers for White Leathers

Frequently pickled sheepskins are split into grain layers, called *skivers*, and flesh layers used for making chamois leather. The skivers are used for hat bands, bookbinding and many other purposes. One method of tanning for whites is as follows: Put 1000 lbs. pickled weight into a tanning drum, add 80 lbs. of salt in 100 gals. of water at 80° F. and run for 5 min. to open them up and take the creases out. Drain and add 50 lbs. of salt in 50 gals. of water at 80° F. and run 5 min. Then add 16 gals. of stock Tanolin-W2XD liquor and run 30 min. Add 16 gals. more of the stock Tanolin-W2XD liquor and run 2 hours. Dissolve 9 lbs. of soda ash in 9 gals. of water. Add 3 gals. and run 30 min.; add 3 gals. more and run 30 min.; then add the remaining 3 gals., run 60 min. and drain. Wash in running water at 90° F. for 10 min., then at 120° F. for 5 min., and drain. Dissolve 40 lbs. of starch in 30 gals. of boiling water, cool to 125° F. and stir into it 15 lbs. of Colloidal Clay-A (Saxe-Rushworth Co.) and 7½ lbs. of titanium dioxide. Add to the drum and run 20 min. Then add 90 lbs. of Acidolene-N-14-B (Martin Dennis Co.) in 50 gals. of water at 125° F., run 30 min. and pile on horses.

All the foregoing procedures may be applied to practically any type of pickled stock. For example, kangaroo skins may be tanned exactly like goatskins by either the one-bath or two-bath processes. With hogskins, it is necessary merely to make sure that the chrome has completely penetrated the stock before adding the soda ash solution; and then to add soda ash according to the precipitation figure, increasing both pH value and time of tanning according to the degree of softness desired in the leather.

Effect on Chrome Tanning of Adding Salts of Organic Acids

Before tanners learned how to control the manufacture of one-bath chrome liquors by reducing sodium dichromate with sugar and acid, chrome liquors were sometimes obtained that had no tanning properties at all, regardless of the amount of alkali added; in fact, such liquors could be made alkaline and no precipitation of chrome would occur. Procter and Wilson investigated this in 1915, and found that the trouble arose from organic acids that are produced during the oxidation of the sugars by the sodium dichromate. They showed that the addition of large amounts of salts of organic acids to a chrome liquor destroyed its tanning properties and prevented the precipitation of chrome upon the addition of alkali. In fact, they showed that fully chrome-tanned leather could be completely detannized and converted into raw collagen by treatment with salts of organic acids.

This discovery naturally attracted a great deal of attention and resulted in much research work on the effect on chrome tanning of different kinds of organic acids and their salts. It was found that these salts form exceedingly complex chemical compounds with basic chromic sulfate and markedly alter its tanning properties. By adding increasing amounts of such salts, it was found that the pH value at which precipitation of the chrome occurs increases until it will not precipitate upon the addition of any amount of alkali. However, when this point

is reached, the chrome liquor loses all its tanning properties. At the same pH value, chrome concentration, temperature and time of tanning, the fixation of chrome by hide substance decreases with increasing amounts of such salts added. If, on the other hand, for each small addition of the organic-acid salts, soda ash is added to keep the pH value at a point just under that at which precipitation takes place, more chrome can be fixed in some cases than if no organic-acid salt was added. Using these salts in this way, leather can be produced that is fuller and that provides a greater thickness and area yield that is very desirable. Many tanners use sugars in making their chrome liquors because of the effects of the organic acids which are formed as a by-product. Because it is exceedingly difficult to control the formation of organic acids in the reduction of sodium dichromate with sugars, the writer has preferred to make the chrome liquor with sulfur dioxide and then to add the specific organic-acid salts that give the best results. In the writer's experience, one of the most advantageous salts to use is sodium formate. A description of its use follows.

Tanning Calfskins with Chrome Formate Liquor

Take the calfskins directly from the bate, without pickling. Put a pack of 1000 lbs. bated weight into the tanning drum. To 30 gals. of the stock sulfur dioxide chrome liquor (containing the reaction products of 2 lbs. of sodium dichromate per gal.) add 55 lbs. of sodium formate dissolved in 30 gals. of water and mix well. To the stock in the drum, add 40 gals. of water at 80° F., start the drum running and add the chrome-formate liquor at 80° F. When the skins have been completely penetrated by the chrome, as shown by examing cuttings, start adding 15 lbs. of soda ash dissolved in 20 gals. of water at 80° F., taking 1 hour to add. Run for 1 hour after all the soda ash has been added and measure the pH value of the liquor. If it is 5.2 or higher, drain off the liquor and wash the stock in running water at 70° F. for 1 hour, haul out and send to be set out and shaved. If the pH value is less than 5.2, raise it to this value by the cautious addition of soda ash, and then proceed to drain and wash.

Some tanners prefer to tan the stock over night because in this way they more nearly exhaust the chrome liquor and get a correspondingly greater fixation of chrome. The writer has tanned light calfskins by this method so that they would stand the boiling test only 30 min. after adding the chrome liquor and without the addition of any soda ash. The finished leather made by this rapid process was excellent. As a rule, a more economical use of materials can be made by keeping the stock in the liquor over night. However, in times of forced production, the capacity of the plant can be greatly increased by using the rapid method.

When using this method for heavy steerhides for sole leather, if the stock has not been thoroughly delimed, the pH value may be raised to such point that penetration of the chrome into the thickest parts of the stock may take as long as 24 hours. By using pickled stock, the rate of penetration is greatly increased, but the pH value must be raised to a higher level.

Comparing calfskins tanned by this procedure with those tanned by the procedure given first in the chapter, we find that this use of sodium formate has made the final leather fuller and plumper; its chromic oxide content has been increased by one-half and it gives up water more rapidly. When the stock is set out after coloring and hung to dry in the same drying tunnel under the same conditions, the chrome formate leather dries in about one-quarter of the time required for the leather without formate.

The application of the chrome formate tannage to all types of raw stock is evident from the descriptions of the regular tannage given above.

At this point in the chapter, we have completed our descriptions of practical procedures in chrome tanning. Before proceeding to some of the more scientific aspects of chrome tanning, it seems desirable to say something about the materials used in the construction of drums and paddle vats used in chrome tanning.

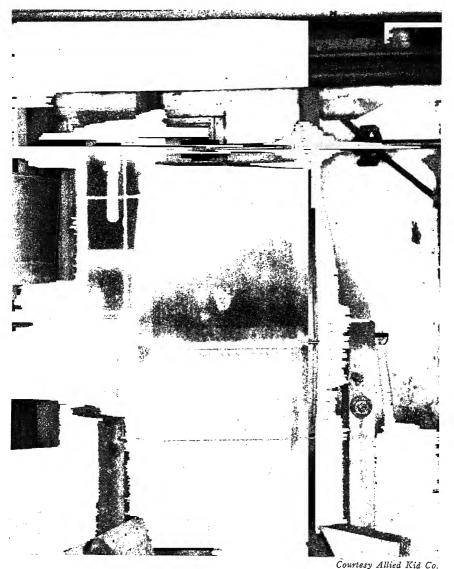
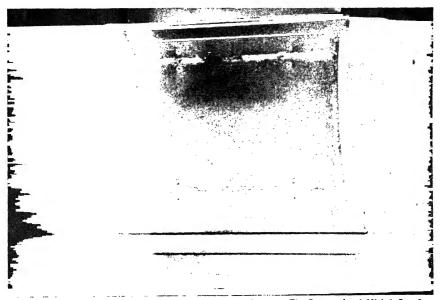


Fig. 226. Solid Inconel Drum Used for Chrome Tanning Goatskins.

Materials Used in the Construction of Drums and Paddle Vats

In most chrome-tan yards, the drums and paddle vats are made of wood, such as cypress or redwood, held together with brass bolts. Sometimes iron bolts are used, their heads being heavily copper-plated where contact is made with the liquors inside of the drum. Great care is usually exercised to avoid any contact of iron with the acid liquors used in pickling and chrome tanning.

The rapid corrosion of iron by the acid liquors causes great losses, not only because of the necessity of frequent replacement, but because the liquors become contaminated with iron and may cause serious discolorations of the finished leather. Moreover, corroded bolt heads inside the drum may develop sharp edges that will scratch the skins during the running of the drum, and losses from this source might become very heavy before they were discovered. The hollow gudgeon and plates inside the drum where contact is made with the liquor should never be made of iron.



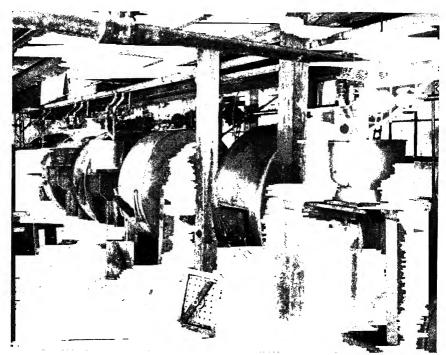
Courtesy The International Nickel Co., Inc.

Fig. 227. Inside of Wooden Drum Lined with Inconel Metal.

Curiously enough, the one-bath chrome liquors seem to have no deleterious effect upon wood, but rather a marked preservative action. On the other hand, pickle liquors and the acid dichromate liquors used in the two-bath tannage are so destructive of wood that the equipment must occasionally be replaced.

Probably the most corrosive liquor used in the tannery is the first bath of the two-bath process. The corrosive action of the acid is greatly increased by the oxidizing action of the dichromate. In tests conducted under plant operating conditions where the two-bath process was in use, it was found, of course, that iron could not be used at all. The corrosion rate for yellow brass was 0.139 inch per year, and the brass became dezincified. For copper, it was 0.039 inch per year and for Monel metal (an alloy of nickel and copper), it was only 0.006 inch per

year. Recently a new alloy has become available for tannery use under the name of Inconel. It is an alloy of nickel and chromium and it is much more resistant to corrosion than even Monel metal. In a test on the long storage of sulfonated oils, it was found that the corrosion rate for Monel metal was only 0.00036 inch per year, but for Inconel it was only 0.000025 inch.



Courtesy Allied Kid Co.

Fig. 228. Battery of Drums Used for Chrome Tanning Goatskins.

All-metal tannery drums of Inconel are now being used in a number of tanneries, apparently with great success. Such a drum is shown in Fig. 226 being used for chrome tanning goatskins. Although the initial cost of such drums is higher than that of wooden drums, they eventually pay for themselves. They are of much lighter construction than the wooden drums and save in power requirements. There is practically no corrosion to require replacements. The inside always remains smooth, to insure the stock against the development of rough edges and scratching. Unlike wood, the metal is non-absorbent, and the same drum can be used for any operation in the tannery. After being used for dyeing black leather, a drum can readily be cleaned and used at once for tanning white leather.

In order to avoid the initial cost of all-metal drums, some tanners are having their wooden drums completely lined inside with Inconel. Such a lining is shown in Fig. 227. The lining is of 0.062-inch standard sheet welded into the drum in position. This drum is 8 ft. in diameter by 5 ft. wide and equipped with shelves instead of the usual pegs for lifting the stock.

Wooden paddle vats are lined in the same way with Inconel. This metal is so resistant to corrosion that many tanners are finding it desirable to use measuring pails made of it and to use it wherever corrosion is annoying.

Fig. 228 shows a battery of drums used in chrome tanning goatskins. The two to the right are made of Inconel and the others of wood. These are the first solid Inconel drums to be used in a tannery.

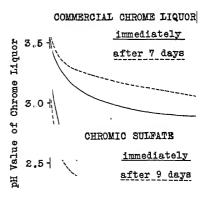
General Properties of One-bath Chrome Liquors

The chemistry of chrome tanning is exceedingly complex. Out of the vast amount of work done on the chemistry of chrome tanning have come many facts with which the tanner with no knowledge of chemistry can and should become familiar, because a knowledge of the available facts will enable him to operate his plant more efficiently and guide him in making valuable improvements. Many of the graphs presented were prepared for chemists; but, as this book is written for readers with no knowledge of chemistry, wherever scientific terms appear, they will be interpreted in the language of the layman.

Effect of Concentration of Chrome Liquor on Its pH Value

Where the term "commercial chrome liquor" is used in what follows, it refers to the basic chromic sulfate manufactured and sold by Martin Dennis Co. under the name of *Tanolin-T*. Comparative results are given for pure chromic sulfate, which has no basicity (or an acidity of 100 percent). The expression "120 grams Cr₂O₃ per liter" means that the chromic oxide content of the chromic sulfate or basic chromic sulfate in the liquor is equal to 1 lb. per gallon.

Fig. 229.
Effect of Concentration of Chromic Sulfate and of Tanolin and also of Time on the pH Values of the Chrome Liquors.



10 20 30 40 Grams Cr_2O_3 per Liter

Thomas and Baldwin made a long series of studies of the effects of various treatments of chrome liquors upon their pH values. Fig. 229 shows the effect of increasing concentrations of pure chromic sulfate and of Tanolin upon the pH values of the liquors and the further change of pH values with time. Both materials being acid, increasing their concentrations causes an increase in acidity; that is, a lowering of pH value. Since the pure chromic sulfate had no basicity,

or an acidity of 100 percent, it naturally lowered the pH value more than Tanolin, which had a basicity of 40 percent, or an acidity of 60 percent. The continuous lines show the pH values taken immediately after the substances dissolved, before time enough was allowed for equilibrium to be established. The broken lines show the pH values taken after the liquors had stood for 7 or 9 days, as indicated on the graphs. The pure chromic sulfate slowly continues to hydrolyze (react chemically with water), forming basic chromic sulfate and liberating free sulfuric acid, which gradually lowers the pH value. The Tanolin, being initially very basic, also hydrolyzes, but it tends to form a less basic chromic sulfate by combining with sulfuric acid and raising the pH value.

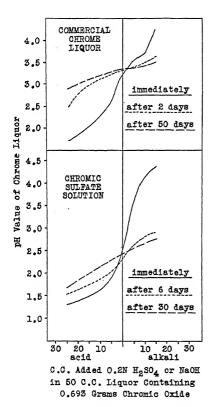


Fig. 230.

Effect of Adding Acid or Alkali to Chrome Liquors upon Their pH

Chrome Liquors upon Their pH Values and the Subsequent Changes in pH Value with Time.

Effect of Adding Acid or Alkali to a Chrome Liquor on Its pH Value

Thomas and Baldwin next turned their attention to the effect of adding sulfuric acid (H₂SO₄) or caustic soda (NaOH) to chrome liquors upon the pH values of the liquors and upon the subsequent changes in pH value with time of standing. Each chrome liquor had a strength equivalent to 11½ lbs. of chromic oxide in 100 gals. In Fig. 230, the addition of 10 cc. of 0.2N H₂SO₄ in 50 cc. of liquor containing 0.693 gram of chromic oxide means the same as the addition of 1½ lbs. of chromic oxide. The addition of 10 cc. of 0.2N NaOH in 50 cc. of liquor containing 0.693 gram of chromic oxide means the same as the addition of 1½ lbs. of

pure caustic soda to 100 gals. of chrome liquor containing 11½ lbs. of chromic oxide. The pH values of the commercial Tanolin liquors are all higher than those of the corresponding liquors of pure chromic sulfate. In both, the addition of increasing amounts of acid causes decreasing pH values, as would be expected.

The very significant fact is that the pH values continue to change for a long time after the addition of alkali. If acid has been added, the chromic salt slowly removes acid from solution, making itself less basic, and raising the pH value of the liquor. If caustic soda has been added, the chromic salt slowly gives up acid, making itself more basic, and lowering the pH value of the liquor. It should be emphasized that such slow changes always take place after any addition of acid or alkali to a chrome liquor. In fact, they take place after dilution or the addition of any material to a chrome liquor.

Changes in the basicity of a chromic salt cause changes in the properties of leather tanned with it. If a chrome liquor is made up and used immediately, it will produce leather of slightly different characteristics from the leather that would be produced from the same liquor after standing for a day before use. When soda ash is added to a chrome liquor during tanning to raise the pH value, it will be found that the pH value will fall again after the addition. This is shown in Fig. 215. Probably no true equilibrium is ever established in chrome tanning, but these facts show the necessity for keeping all variable factors the same during tanning, if uniform results are to be expected.

Effect of Adding Neutral Salts to a Chrome Liquor on Its pH Value

Thomas and Baldwin then turned their attention to the effect of adding different neutral salts to chrome liquors upon the pH values of the liquors and upon the subsequent changes in pH value with time of standing. It may be wondered why a salt, being neutral, should either raise or lower the pH value of a solution. Common salt (sodium chloride) is neutral, but if added to an acid solution, it will lower its pH value. Glauber's salt (sodium sulfate) is also neutral, but if added to an acid solution, it will raise its pH value. These effects take place in pure solutions of hydrochloric acid with no chromium salts present. When chromic salts are present, the effect is complicated by the changes that take place in the chromic salts.

Fig. 231 shows the effect of adding different salts to liquors made from Tanolin and those made from pure chromic sulfate. The term "moles salt per liter" means the molecular weight of the salt taken in grams and dissolved in water to make a solution having a volume of 1 liter. The tanner can readily convert moles per liter into lbs. per gal. as follows. Various handbooks of chemistry are available which give the molecular weights of different substances. By looking up sodium chloride, he will find that it has a molecular weight of 58.45. This means that a solution containing 1 mole per liter contains 58.45 grams per liter. A solution of 1 lb. per gal. is the same as one of 120 grams per liter. Dividing 58.45 by 120, we get 0.487. A solution containing 1 mole of sodium chloride per liter thus contains 0.487 lb. per gal.

A tanner may buy sodium sulfate in two different forms, anhydrous Glauber's salt (Na₂SO₄), which has a molecular weight of 142.05, and crystalline Glauber's salt (Na₂SO₄.10H₂O), which has a molecular weight of 322.21. In order to make a solution of 1 mole of sodium sulfate per liter, it is thus necessary to add either 1.184 lbs. of anhydrous Glauber's salt or 2.685 lbs. of crystalline Glauber's salt per gal. Ammonium sulfate and magnesium sulfate were included in the tests merely to get a better understanding of the chemistry of the changes. All solu-

tions contained 13.86 grams of chromic oxide per liter, or 0.115 lb. per gal. Adding increasing amounts of common salt (sodium chloride or NaCl) results in a steadily decreasing pH value, both in the Tanolin and pure chromic-sulfate solutions. Upon standing for 30 days, chromic-sulfate solutions increase in pH value, because the chromic sulfate is taking sulfuric acid from the solution to make itself less basic. In the case of the Tanolin, at lower concentrations of salt, the pH values rise because the chromic sulfate is taking acid from the solution to become less basic. At higher concentrations of salt, the pH values decrease with time because the chromic sulfate is giving up acid to the solution, making itself more basic.

When increasing amounts of Glauber's salt are added to the Tanolin liquor, the pH value rises until it reaches a point of maximum and then decreases. The rise in the curve is due primarily to the effect of sodium sulfate on acid solutions, but the fall is due to complex chemical reactions between the sodium sulfate and the chromic sulfate.

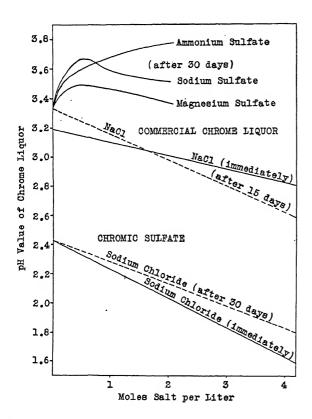


Fig. 231.

Effect of Adding Different Kinds and Amounts of Neutral Salts to Chrome Liquors on Their pH Values and the Subsequent Changes in pH Value with Time.

In order to show the nature of the change of pH value of the Tanolin liquor with time after the addition of 0.974 lb. common salt per gal., the data shown in Fig. 232 were obtained.

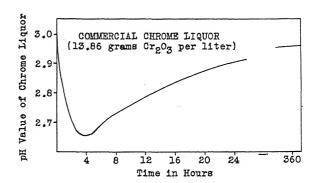
Even 15 days after the salt was added, changes are still going on, and these are reflected in the changing pH value.

Effect of Concentration of Chrome Liquor on Fixation of Chrome by Hide Substance

Studies of the effect of concentration of Tanolin liquors upon the lixation of chrome by hide substance have been made by Baldwin and by Thomas and Kuly; using hide powder for the experiments.

Fig. 232.

Change of pH Value of Tanolin Liquor with Time After the Addition of 0.974 lb. of Sodium Chloride per Gal.



In each test an amount of hide powder containing 5 grams of hide substance was put into a wide-mouth bottle and covered with 200 cc. of Tanolin liquor containing a definite amount of chromic oxide. The bottle was shaken at intervals for 48 hours and then the tanned powder was washed free from soluble matter, dried and analyzed, and the pH value of the used liquor measured.

No materials were used except the hide powder and Tanolin liquor, and no attempt was made to control the pH value of the liquors. In order to make the results more readily intelligible to the tanner, the writer has drawn the new chart shown in Fig. 233.

With increasing concentration of chrome, the percentage of chrome fixed by the hide substance increases to a maximum and then decreases with further increase in concentration. Fig. 229 shows that the pH value of Tanolin liquors decreases with increasing concentration of the Tanolin. In Fig. 233, the pH values of the used liquors have been inserted for the tests at higher concentrations than that at which maximum fixation of chrome took place. Since chrome fixation decreases rapidly with decreasing pH value, it is clear that a large part of the decreasing fixation of chrome at greater concentrations must be attributed to the decreasing pH value of increasing concentration of Tanolin. It is interesting to note that maximum fixation of chrome occurs at about the concentration of chrome and pH value that are commonly used in chrome tanning.

Effect of Added Salts on Chrome Tanning

Although the addition of sodium sulfate to an acid solution raises the pH value and the addition of sodium chloride lowers it, Wilson and Gallun showed that the addition of either salt to a chrome liquor decreases the fixation of chrome by hide substance. Thomas and Foster studied this action in a series of tests with hide powder. They used a pure chrome liquor made by reducing sodium dichromate with sulfur dioxide. Portions of hide powder containing 5 grams of hide substance each were placed in wide-mouth bottles, covered with 50-cc. portions of water and allowed to soak over night. Either sodium chloride or sodium sulfate was added to give the final concentrations desired, and then 150-cc.

portions of the chrome liquor were added to give final concentrations of chrome equal to 12.9 lbs. of chromic oxide per 100 gals. The bottles were shaken for 48 hours and then the tanned powders were washed free from soluble matter, dried and analyzed, and the pH values of the liquors were measured.

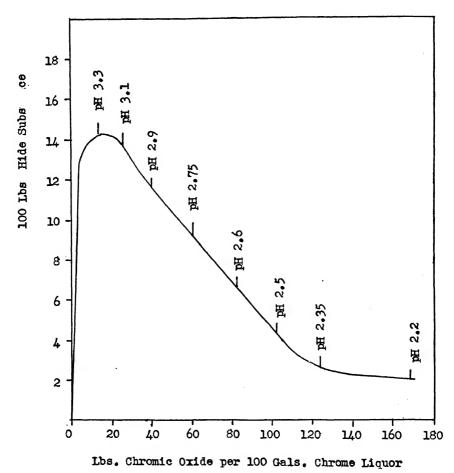


Fig. 233. Effect of Concentration of Tanolin Liquors on the Fixation of Chromic Oxide by Hide Powder in 48 Hours.

The results are shown in Fig. 234. The pH values shown on the chart are those of the liquors taken after tanning. Increasing concentrations of either salt decrease the fixation of chrome by hide substance very markedly. The effect of sodium sulfate is greater than that of sodium chloride in spite of the fact that sodium sulfate actually raises the pH value of the chrome liquor. The effect of the added salt upon the pH value of the liquors undoubtedly has much to do with the final result, but the added salts not only alter the pH value, but produce other effects that rank in importance with pH value. For example, the writer has found that the addition of neutral salts to a chrome liquor increases the amount of

alkali required to start precipitation of the chrome. It also necessitates increasing the pH value of the chrome liquor in order to get the same amount of chrome fixed by the hide substance.

Effect of pH Value and of Added Salts on Chrome Tanning

In order to show how the effect of pH value on chrome tanning is influenced by the addition of various salts, the writer carried out a series of experiments in which 10-gram portions of air-dry hide powder (each containing 8.7 grams of hide substance) were tanned for 24 hours in 100-cc. portions of chrome liquor to which different kinds and amounts of salts had been added. The chrome liquor was made by reducing sodium dichromate with sulfur dioxide. This was used in all tests except No. 1, where it was desired to get the effect with no salt present. The liquors for the No. 1 series were made by adding barium hydroxide in different proportions to solutions of pure chromic sulfate. The barium hydroxide precipitated the sulfuric acid from the chrome liquors, leaving in solution only a series of pure

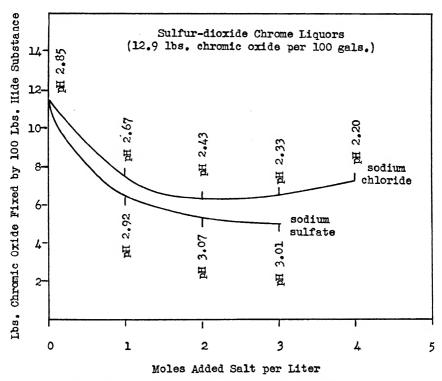


Fig. 234. Effect of Added Salts on the Fixation of Chromic Oxide by Hide Powder in 48 Hours.

basic chromic sulfates increasing in basicity from 16 to 36 percent. These liquors contained no salt other than the basic chromic sulfate; only the liquors freed from the barium sulfate were used.

In making chrome liquor from sodium dichromate and sulfur dioxide, for each pound of chromic oxide there is formed 0.93 lb. of sodium sulfate. This salt was

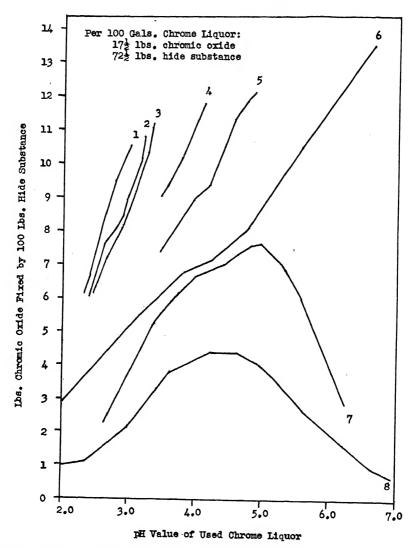


Fig. 235. Effect of Added Salts and of pH Value on the Fixation of Chromic Oxide by Hide Powder in 24 Hours.

Per 100 gals. chrome liquor:

- 1. no salt (sodium sulfate removed).
- 2. 25.6 lbs. sodium chloride.
- 3. 51.2 lbs. sodium chloride.
- 4. 12.8 lbs. sodium chloride, 14.9 lbs. sodium formate.
- 5. 25.6 lbs. sodium chloride, 29.8 lbs. sodium formate.
- 6. 59.6 lbs. sodium formate.
- 7. 44.0 lbs. sodium oxalate.
- 8. 58.7 lbs. sodium oxalate.

left in the liquors of all other series. In each test of each series, the 100 cc. of chrome liquor was made to contain 2 grams of chromic oxide, which is the equivalent of 17½ lbs. of chromic oxide per 100 gals. of liquor. This means that all liquors, except those of series No. 1 contained the equivalent of 16.3 lbs. of sodium sulfate per 100 gals. in addition to the added salts as indicated in Fig. 235.

In each test of each series, exactly 10 grams of air-dry hide powder containing 8.7 grams of actual hide substance was shaken with 100 cc. of chrome liquor for 24 hours. This is equivalent to 72½ lbs. of hide substance per 100. gals of liquor. Approximately this amount of hide substance is contained in 360 lbs. pickled weight of calfskins.

After tanning, the tanned powders were washed in running distilled water for 24 hours to free them from soluble matter. They were then dried and analyzed for chromic oxide and hide substance. The results are shown in Fig. 235.

The amounts of salts indicated in Fig. 235 were added before the dilutions were made to final volume. The adjustments of pH value were also made before the final dilution, using caustic soda or sulfuric acid, as required. No such adjustments had to be made for series No. 1, because this was taken care of in the addition of barium hydroxide. In series No. 1 to No. 6 inclusive, the highest point on each curve represents the pH value above which precipitation of the chrome took place.

The results are so important to any chrome tanner that he should study them with great care and thoroughness. At a pH value of 3.0, the greatest fixation of chrome occurs in the liquor containing no salt, but the pH value of the liquor cannot be raised above 3.0 without causing precipitation of the chrome. Series No. 2 represents the average salt content when using the procedure for calfskins described first in this chapter. At a pH value of 3.0, only 9.2 lbs. of chromic oxide is fixed by 100 lbs. of hide substance as against 10.6 lbs. where no salt is present. However, the pH value can be raised to 3.2 before precipitation takes place and, at this pH value, 10.8 lbs. of chrome is fixed. When the amount of added salt is doubled, as in series No. 3, the precipitation point is raised to 3.3, at which point 11.2 lbs. of chrome is fixed; many tanners have this amount of salt in their liquors because they add salt in addition to that introduced by the pickled stock.

From the first three series, we derive the general rule that, when the salt concentration is increased, the pH value can and should be raised to a higher point in order to get the same fixation of chrome, and that the fixation of chrome can be still further increased by raising the pH value to a point just under that at which precipitation begins.

The effect of adding sodium formate is much greater than that of adding sodium chloride. Series No. 6 has a content of sodium formate equivalent to the content of sodium chloride in series No. 3. At a pH value of 3.0, the fixation of chrome from the formate liquor is only 5.2 lbs. as against 8.8 lbs. from the chloride liquor. However, the pH value of the chloride liquor can be raised only to 3.3 before precipitation starts, but the pH value of the formate liquor can be raised to 6.6. At the pH values just under the precipitation points, the fixation of chrome from the chloride liquor is only 11.2 lbs. as against 13.5 lbs. from the formate liquor.

In series No. 7 and No. 8, where sodium oxalate was used, no precipitation of chrome took place at any pH value. As the pH value is increased, increasing fixation of chrome occurs until points of maximum are reached beyond which the fixation of chrome decreases. As the concentration of sodium oxalate is greatly increased, there is a decreasing fixation of chrome. In very concentrated solu-

tions, practically no tanning takes place and sodium oxalate can actually be used to detannize chrome leather.

This work formed part of a research that the writer carried on for Victor Chemical Works, Chicago, to whom the writer is indebted for permission to publish the results.

Effect of Time and Temperature on Chrome Tanning

In all the foregoing experiments, where no mention is made of temperature, the tests were carried on at room temperature, usually about 70° F. Nevertheless, a change of temperature of as much as 5° F. produces measurable changes in composition of the leather produced. In 1929, H. B. Merrill carried out a series of experiments under the writer's direction to determine the effect of temperature of the chrome liquor upon the tanning of pickled calfskin. The calfskin used was pickled as described in Chapter 9. From the choicest part of the skin, 25 strips 2×6 inches were cut, every effort being made to have them as nearly alike as possible. Each piece was trimmed before tanning to have a pickled weight of exactly 30 grams. A stock solution of Tanolin-T liquor was made up to contain 15 grams of chromic oxide per liter, or 12½ lbs. per 100 gals. This was allowed to age for a week and then 2-liter portions were placed in each of 5 wide-mouth bottles, which were placed in thermostats at temperatures of 50°, 68°, 86°, 104°, and 122° F., accurate to about 0.02° F. On the day following the entry of the liquors into the thermostats, 5 strips of pickled calfskin were put into each liquor. During the first day, each liquor was agitated every fifteen minutes, after which they were agitated twice each day.

At the end of 4 hours, from each liquor were taken one strip and 400 cc. of liquor. This was repeated at the end of 8, 24, 48 and 120 hours. Upon being taken from a liquor, each strip was washed for an hour in running tap water. A piece was taken off for the boiling test and the rest was dried and analyzed for chromic oxide, hide substance and acid sulfate, from which the basicity of the chromium salt fixed by the hide substance was calculated. The used liquors were analyzed for chromic oxide, basicity and pH value. The strips tanned at 122° F. were very slightly affected by boiling for 5 minutes after tanning for only 4 hours, but all the others shrank very badly. After tanning for 8 hours, the strips tanned at both 122° F. and 104° F. stood the boiling test perfectly, but the others shrank badly. After tanning for 24 hours, the strips from the liquor at 86° F. also stood the boiling test, but those at 68° F. and 50° F. did not. At the end of 48 hours, all strips stood the boiling test.

The volume of liquor per unit weight of skin was made large so as not to introduce any marked change in the composition of the liquors during tanning. There was present only 62½ lbs. pickled weight per 100 gals. of chrome liquor. The original liquor contained 12½ lbs. of chromic oxide per 100 gals. This dropped in 120 hours to 10.7 lbs. at 50° F., to 10.5 lbs. at 68° F., to 9.8 lbs. at 86° F., to 9.7 lbs. at 104° F. and to 9.6 lbs. at 122° F.

The pH values changed but little. The pH value of the original liquor was 3.23. It changed in 120 hours to 3.14 at 50° F., to 3.20 at 68° F., to 3.22 at 86° F., to 3.20 at 104° F. and to 3.14 at 122° F.

The original basicity of the chrome liquor was 49 percent. It changed to 58 percent at 50° F., to 55 percent at 68° F., to 49 percent at 86° F., to 48 percent at 104° F. and to 50 percent at 122° F.

Fig. 236 shows the effect of temperature and of tanning time on the fixation of chromic oxide by pickled calfskin. The greatest percentage increase in chrome fixation with temperature rise from 50 to 122° F. occurs in the 8-hour tannage,

where the chrome fixed at 122° F. is nearly four times that at 50° F. Fig. 237 shows the same data rearranged to show tanning as a function of time.

Fig. 238 shows the data rearranged to show the number of hours required for the fixation of 8 lbs. of chromic oxide per 100 lbs. of hide substance. Raising the temperature from 50 to 122° F. reduces the tanning time from 42 hours to only 5 hours.

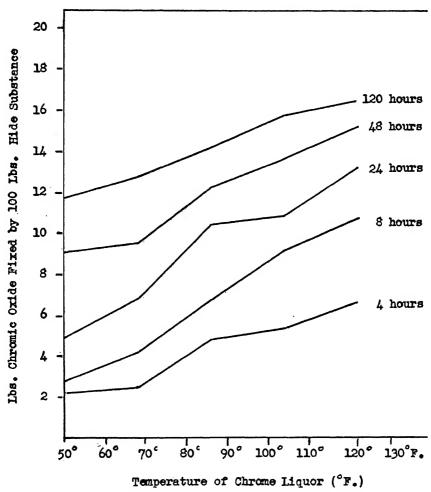


Fig. 236. Effect of Temperature and Tanning Time on Fixation of Chromic Oxide by Pickled Calfskin.

The basicity of the chromium salt fixed by the hide substance has a very marked influence over the subsequent operations and over the properties of the finished leather. The effect of temperature and of tanning time upon the basicity of the chromium salt fixed by the hide substance is shown in Fig. 239. In these experiments, it must be remembered that no alkali was added to the liquors during

the tanning. Although the original basicity of the chrome liquor was 49 percent, the pickled skin contained free sulfuric acid in quantity sufficient to convert the 49 percent basic chromic sulfate which penetrated the skin and combined with the hide substance in 4 hours at 50° F. into a salt 31 percent more acid than pure

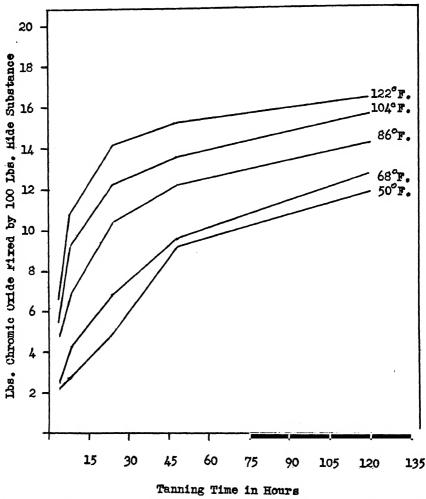


Fig. 237. Effect of Tanning Time and Temperature on Fixation of Chromic Oxide by Pickled Calfskin.

chromic sulfate. This is indicated on the chart as a basicity of -31 percent, equivalent to an acidity of 131 percent. The penetration of chromic salt into the skin increases with both time and temperature, until after 120 hours at 122° F., we get a large amount of chrome fixed having a basicity of 66 percent. Under most tanning conditions, the chromic salt fixed by the hide substance is more basic than that present in the liquor. Where the differences in basicity are large, the

curves in Fig. 238 conform to the rule that the basicity of the chromic salt fixed increases with tanning time and temperature. The basicity also depends upon penetration and contact of the chromic salt with the hide substance. The thickness and density of a calfskin vary greatly over its area and this, in turn, affects the

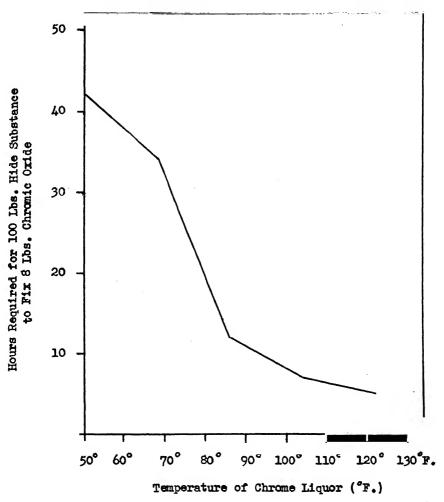


Fig. 238. Effect of Temperature of Chrome Liquor upon the Number of Hours Required for 100 Lbs. Hide Substance of Pickled Calfskin to Fix 8 Lbs. of Chromic Oxide.

rate of penetration of the chrome. Such differences in the strips of calfskin used in the experiments may well be responsible for the crossings of the curves at temperatures above 68° F. and tanning times greater than 8 hours.

During the running of a drum in practice, a considerable amount of mechanical heat is developed, which increases with the diameter of the drum and number of revolutions per minute. In different tanneries, drums of different sizes and speeds

are used and, with the same procedure, leathers of different composition and properties are produced. As a rule, when the temperature of the chrome liquor initially is 70° F., it will rise during tanning to some point between 100 and 120° F. because

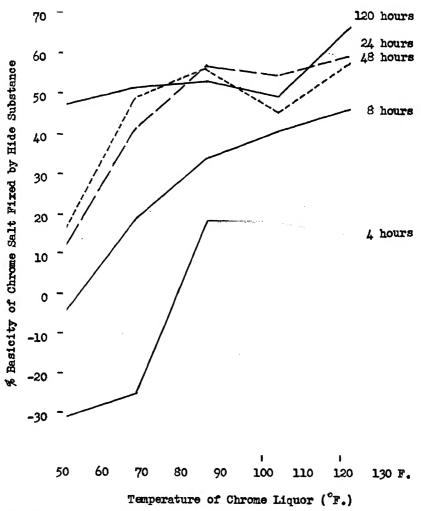


Fig. 239. Effect of Temperature and Tanning Time on Basicity of Chromic Salt Fixed by Pickled Calfskin.

of the development of mechanical heat and the heat liberated by chemical reactions. Decreasing the speed of a drum from 18 to 16 revolutions per minute is sufficient to produce changes in the characteristics of the finished leather readily noticeable to the average assorter.

In many tanneries, where the chrome liquor is made with sulfur dioxide and no salts of organic acids are added, the basicity of the chromium salt fixed during tanning ranges from 40 to 60 percent, with an average of 50 percent. In the subsequent operations, the basicity is usually raised from 50 to 70 percent, with an average of about 60 percent. When salts of organic acids are used, measurements of basicity become exceedingly complex and their interpretations become matters of speculation.

Throughout this book, the writer has tried to provide the tanner with the minimum amount of information that he should have to operate his tannery successfully. Practical tanning consists of series of exceedingly complex chemical reactions, but the writer has avoided chemical discussions in the interest of clarity to the tanner with no training in chemistry. For this reason, much of the work done on the chemistry of chrome tanning has been omitted. However, references are given at the end of this chapter to publications that will be very helpful to many tanners desiring a deeper insight into the many problems involved in chrome tanning.

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Chapter 13

Miscellaneous Tannages

Probably well over 90 percent of all leather is tanned either with vegetable tannins or with basic chromium sulfate, or with combinations of the two. There are many other classes of substances capable of converting raw hide into leather; but they are not used so extensively as chromium sulfate or the vegetable tannins, either because their cost is greater or because they do not produce properties desired in most leathers nor give yields of leather that are economical. As each kind of tanning material imparts special properties to leather, combinations of different tannages are often used to obtain properties desirable for special purposes. Some of these other classes of tanning materials are used in conjunction with both chromium sulfate and the vegetable tannins to effect an improvement in certain properties of vegetable-tanned or chrome-tanned leathers, or economies of operation.

Chrome Retanning

Chrome tanning has the great advantage over vegetable tanning for the tanner in the short time required to produce leather, but the great disadvantage in producing a much lower yield of leather. Chrome-tanned leather has a much greater resistance to heat and to abrasion than vegetable-tanned leather. On the other hand, vegetable-tanned leathers are fuller and plumper and give much greater yields of leather from the same hides. Vegetable-tanned leathers change less in area with changing relative humidity; they lend themselves better to tooling and embossing; and they are less affected by perspiration. The advantages and disadvantages for the two kinds of tannage can be averaged by using both. Usually the stock is first chrome-tanned because it is done more quickly than vegetable tanning, and then the stock is retanned with vegetable tannins. This is known as *chrome retanning*.

Chrome retanning is usually employed for work-shoe upper leather, for sport shoes and for making the type of leather known as *Elk* from cow sides. The leather is first chrome tanned as described in Chapter 12. After tanning, it is set out, split and shaved according to the methods to be described in Chapter 14. In the shaved condition, it contains about 50 percent of water by weight. A typical retanning procedure for chrome-tanned cow sides to be used for shoe uppers follows:

Make up a stock tan liquor by dissolving 1800 lbs. of solid quebracho extract (63 percent tannin) and 2400 lbs. of spruce extract (25 percent tannin) in water and diluting to exactly 1000 gals. Put a pack of 1500 lbs. shaved weight into a drum, wash in running water at 70° F. for 1 hour, and drain. Then add 225 gals. of the stock tan liquor while the drum is running and continue to run for 2 hours. Haul out the stock, pile on trucks or platforms and let stand over night. Then pile the stock in a hydraulic press like that shown in Fig. 172 of Chapter 11. When the water content of the stock is reduced to about 50 percent, it no longer exudes water. The pressure is then released and the stock is taken out of the press. The stock is then sent on to be stuffed as described in Chapter 15.



Fig. 240. Vertical Section of Chrome-retan Cowhide Leather.

Location: butt.
Thickness of section: 40 microns, or 0.00158 inch.
Magnification: 54 diameters.

In this procedure, the tan liquor is usually practically exhausted during the retanning and is run to the sewer when the stock is hauled out. In different tanneries, the kinds and amounts of vegetable-tanning substances used vary according to the purpose for which the leather is to be used and according to details of the subsequent operations. To produce good leather, it is not necessary for the tannin to penetrate completely through the thickness of the hides, because the leather is already completely tanned with chrome. In fact, some users of this type of leather insist on having a middle layer of the leather showing the green of the chrome, as evidence that the leather is genuine chrome-retan.

Fig. 240 shows a vertical section of chrome-retan cowhide leather used in making the uppers of Army shoes. The chrome-tanned layer through which the vegetable tannins have not penetrated appears as a light band in the picture; it is nearer the flesh side because the leather was split after retanning.

Syntans

In 1912 Edmund Stiasny discovered that new types of tanning materials can be produced synthetically by mixing phenolsulfonic acids with formaldehyde under the right conditions. The products formed are water-soluble, precipitate gelatin from solution and exhibit marked tanning properties. He called these products syntans, a contraction of synthetic tannins. Actually, they are very different from the natural vegetable-tanning substances. They were first manufactured commercially

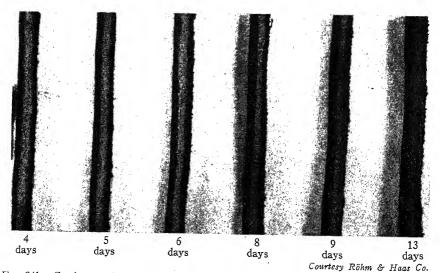


Fig. 241. Cuttings of Bated Cowhide After Being in 30°-Barkometer Quebracho Liquor for Different Lengths of Time.

in Germany by the Badische Soda & Anilin Fabrik division of the I. G. Farben-industrie Aktiengesellschaft under the name of *Neradol*. After thorough and lengthy tests, the first syntan produced in the United States was made by Röhm & Haas Co., who called their product *Leukanol*.

When syntans are used as the only tanning substance, pure-white leathers are produced, but the low yields of leather obtained practically preclude their use for most types of leather. However, they have been found extremely useful in the

making of both chrome and vegetable-tanned leathers and their use today is almost universal.

Leukanol not only penetrates through the thickness of a hide very rapidly, but it increases the rate of penetration of hide by vegetable tannins either when it is added to vegetable-tan liquors or when the hides are pretanned with Leukanol. In addition, it increases the solubility of vegetable-tanning materials and prevents

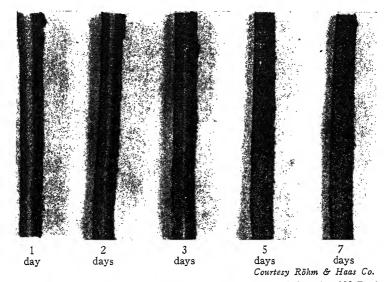


Fig. 242. Cuttings of Leukanol-pretanned Cowhide After Being in 30°-Barkometer Quebracho Liquor for Different Lengths of Time.

the loss of tannins otherwise precipitated as sludge. In sole-leather tanning, the time of tanning can be greatly reduced by pretanning the stock with from 15 to 20 percent on bated weight of Leukanol. When hides pretanned with Leukanol are put into the yard liquors, the rate of penetration of the tannins is greatly increased, the leather acquires a brighter and more uniform color and actually becomes more heavily tanned and of improved properties.

Fig. 241 shows cuttings taken from a cowhide taken after 4, 5, 6, 8, 9 and 13 days in a 30°-barkometer liquor of quebracho extract. This was a hide taken directly from the bate. Fig. 242 shows a portion of the same hide pretanned with Leukanol and then placed in a 30°-barkometer liquor of quebracho extract. The cuttings were taken after 1, 2, 3, 5 and 7 days in the liquor. At the end of only 1 day the tannins have penetrated as far into the hide as in 5 days when the hide was not pretanned with Leukanol after bating. At the end of 5 days, the Leukanol-pretanned hide is more thoroughly penetrated by tannin than the bated hide after 13 days. The Leukanol-pretanned leather was not only more thoroughly and uniformly tanned, but had many other properties superior to those of leather made without Leukanol. The grain was smoother, finer and more uniform and brighter in color. The fibers showed less tendency to cohere, which made the leather much stronger; the fibers at the cross-section of the break were much longer and did not break short, as is the case when the fibers cohere and cannot readily slide over one another.

Similar effects can be obtained without the pretannage by mixing Leukanol with the vegetable-tanning extracts in making up the stock liquor by mixing about 1 part of Leukanol tannin to 3 parts of vegetable tannin. There are 8 different types of Leukanol with different properties.

Leukanol is the standard syntan used on all classes of both vegetable and chrome leathers. Leukanol-ND contains twice as much tan and much less salt; when used in conjunction with vegetable tanning, it imparts to the leather greater firmness and plumpness, but in bleaching chrome leather, it acts like ordinary Leukanol. Leukanol-NS is designed for heavy vegetable-tanned leathers; it produces plumper leather than ordinary Leukanol and has a greater solubilizing effect on the tanning extracts, but it is not suited for bleaching chrome leather. Leukanol-D is designed for use where the solubilizing effect on the vegetable-tanning extracts is most important and color of the leather of less importance; it is not satisfactory for bleaching chrome leather. Leukanol-Y was designed especially for bleaching chrome leather in the making of white leather. Leukanol-104 possesses more filling power than ordinary Leukanol and has proved useful in the mordanting of chrome leather, particularly of garment leathers. Leukanol-WL possesses outstanding filling and bleaching powers and is used for mordanting chrome leathers to get full and uniform shades of color; its remarkable bleaching and lightfastness make it first choice for making premium white leathers on a chrome base. Leukanol-R is used in the manufacture of utility white leathers where lightfastness and greater fullness and roundness of feel are desired. Tamol-NNO is a neutral product in dry, granular form designed especially for use in dyeing leather to produce uniform coloring, particularly in the production of pastel shades; it is also used in tanning and in mordanting and bleaching chrome leather.

The use of Leukanol in the vegetable tanning of pickled sheepskins was described in Chapter 11. In addition to its beneficial effects upon the tannage, Leukanol disperses the natural greases present in the skins and thus better prepares the leather for the subsequent fatliquoring and dyeing operations. It acts similarly upon the grease in the kidney area of cowhides. It is valuable also in connection with the vegetable tanning of pickled stock and in vegetable tanning in the drum.

Leukanol can also be used to retan vegetable-tanned leather. By drumming the stock with about 10 percent of its wet weight of Leukanol, the color is markedly cleared and brightened and the leather and the properties of the leather are improved as in the use of Leukanol during the tannage.

In making chamois leather from pickled sheepskins, the skins are often split into two layers, the flesh layer being used to make chamois leather and the grain layers, or skivers, being used to make the very thin leathers used in bookbinding, linings, hat bands, etc. A good method for tanning the skivers is as follows:

Into a 1500-gal. paddle vat, put 1380 gals. of water at 70° F., add 50 lbs. of ground Sicilian sumac and 15 lbs. of Leukanol, and mix well. Start the paddle running and add 1000 lbs. of pickled sheep skivers. Run the paddle for 2 hours and let stand over night. Next day haul out the stock and send on for the finishing operations. The used liquor may be used for several successive packs by strengthening each time with fresh sumac and Leukanol. Leather tanned in this way is very light in color and may be made into white leather or dyed to produce delicate, pastel shades.

In Chapter 12, the use of Leukanol was described in making white leather from chrome-tanned stock. Leukanol has a peculiar bleaching action on the color of chrome-tanned leather, turning it to a blue so light that the leather can readily

be converted into white leather. One method of making white leather from chrome-tanned stock without loading it heavily with inert white pigments is as follows:

Tan the stock as described for calfskins in Chapter 12. After washing and setting out, split and shave the stock as described in Chapter 14. Put a pack of 1000 lbs. shaved weight into a drum and wash in running water at 140° F. for 5 min., and drain. Then add 100 lbs. of Leukanol in 80 gals. of water at 140° F., run 1 hour, and drain. Then wash stock in running water at 140° F. for 5 min. and drain. Again add 100 lbs. Leukanol in 80 gals. of water, run 1 hour, drain, horse the stock, and send to be fatliquored as described in Chapter 15.

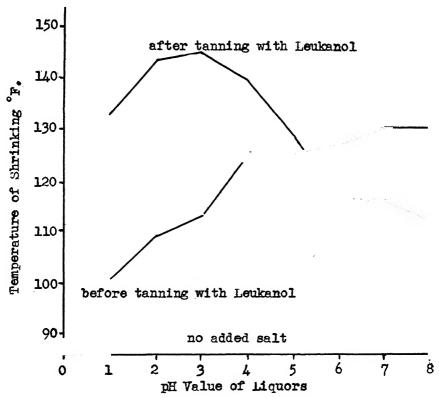


Fig. 243. Effect of pH Value of Liquors Used to Pretreat Goatskins and of Leukanol Liquors Used to Tan Them upon Their Shrink Temperatures.

Leukanol can be used to advantage on all types of leather before dyeing to get more uniform and brighter colors, on chrome-tanned leather before vegetable retanning in order to get a more uniform penetration by the vegetable tannins, and for sole leather in the extracting, oil wheel and dry dip, as described in Chapter 18.

The tanning of skins usually increases their resistance to heat in the wet state. Most chrome-tanned leathers are resistant to the action of boiling water. If leather that will not stand the boiling test is placed in cold water and the temperature is

gradually increased one degree at a time, a point will be reached where the leather suddenly begins to shrink. This point is easily measured with special instruments, and is known as the shrink temperature. The shrink temperature is taken as a measure of the degree of tannage. Theis and Esterly measured the shrink temperatures of goatskins tanned with 5 percent solutions of Leukanol as a function of pH value of the liquors. They used bated goatskins that had been washed, dehydrated with alcohol and acetone, and dried. These were cut into pieces and soaked in water for 24 hours before being used in the tests. A series of solutions was made up with hydrochloric acid and caustic soda to give a range of pH values from 1 to 12. Each piece of goatskin was kept in a solution of definite pH value for 24 hours and then tested for shrink temperature. The results for pH values 1 to 8 are shown in Fig. 243. Another series was treated in the same manner and then treated with 5 percent solutions of Leukanol with pH values adjusted to exactly the same pH values as those of the pretreating solutions, and left in them for 7 days. For example, a piece soaked in a hydrochloric acid solution of pH value of 2.0 for 24 hours was then soaked for 7 days in a 5 percent Leukanol solution with its pH value adjusted to 2.0. After this treatment, the shrink temperatures of the pieces were measured. They are shown in Fig. 243.

The curve marked before tanning with Leukanol represents the raw stock, which is most resistant to heat at pH values between 7.0 and 8.0. At pH values below about 4.7, the Leukanol greatly increases the resistance of the skin to heat, the greatest effect occurring between pH values of 2.0 and 3.0. At pH values above 4.7, the Leukanol-treated pieces are less stable than the raw stock. The conclusion drawn is that Leukanol has very little tanning action at pH values above 4.7 and has its greatest tanning action at pH values between 2.0 and 3.0.

The wide acceptance of the syntans by the American leather industry has induced many other manufacturers to produce them. Among those now available commercially, we might mention *Tanigan* by General Dyestuff Corp., *Tanak* by American Cyanamid & Chemical Corp., *Mertanol* by Monsanto Chemical Co., *Arkotan* by Arkansas Co., and *Tanasol* and *Synektan* by Jacques Wolf & Co.

Alum Tanning

The use of aluminum salts for tanning dates back to ancient times, but they do not combine so readily with the hide protein as do chromic salts or vegetable tannins. Leather tanned with aluminum sulfate alone lacks many of the properties associated with good leather. For this reason tanners of former years referred to the tannage not as tanning, but as tawing. In the tanning of furs, it is important that the hair retain its natural color and not be discolored, as it would be with vegetable tannins or with chromic salts. Aluminum sulfate is colorless and it does not impart any color to skins or to hair.

A very old method of tanning furs was to wash them, flesh them quite clean and then apply to the flesh side a paste made of aluminum sulfate, or common alum, common salt, egg yolk and flour. After these materials had penetrated through the thickness of the skins, they were dried slowly and aged for several weeks. Then they were washed to remove excess salt and coated on the flesh side with a paste made only of egg yolk and flour. They were then dried again and flexed lightly to make them soft. The tanning of shearlings with a combination of aluminum sulfate and chrome alum was described in Chapter 12.

In making some white leathers, including leather for baseball covers, the chief tanning material used is aluminum sulfate. There is no standard procedure for tanning with aluminum sulfate, but the following method will illustrate the

principle: Put into a drum 1000 lbs. of stock pickled as described in Chapter 9. Add 125 lbs. of aluminum sulfate in 80 gals. of water at 70° F. Run drum for 4 hours and then add slowly over 1 hour 30 lbs. of soda ash dissolved in 30 gals. of water and run for an hour longer. Let stand over night. Next morning measure the pH value of the liquor and add enough soda ash solution slowly and cautiously until the pH value is raised to 4.20 with the drum running. After the pH value has reached 4.20, run the drum for an hour longer, haul out the stock without washing and hang to dry. The stock may be kept indefinitely in the dry state without harm.

If the dried stock is then washed with water and given no other treatment prior to fatliquoring, the resulting leather may be hard and tinny. Various methods are employed to overcome this. One is to add to the alumium sulfate solution in the original tanning 20 lbs. of *Tragasol* in 20 gals. of water. Tragasol is a mucilaginous carbohydrate obtained from the endosperm of vegetable seeds. It is marketed by John P. Marston Co. of Boston in the form of a thick jelly, which must be soaked in water over night before use, as it does not dissolve readily. This gives the leather fullness and body, which is very important for some types of white leather.

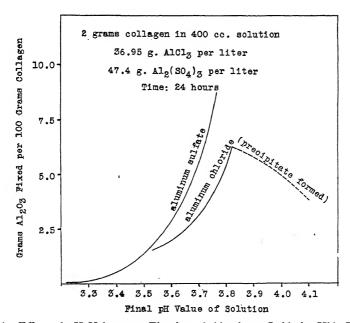


Fig. 244. Effect of pH Value upon Fixation of Aluminum Oxide by Hide Powder.

Another method of preventing the leather from becoming hard and tinny is to retan it with Leukanol. The pack of 1000 lbs. pickled weight is put back into the drum after drying from the alum tannage and given 100 lbs. of Leukanol in 100 gals. water and the drum is run for 4 hours. The liquor is then drained off and the stock washed in running water at 70° F. for 1 hour; it is then sent on to be fatliquored.

Thomas and Kelly studied the effect of pH value on alum tanning using hide powder. They made up a stock liquor containing 47.4 grams of pure aluminum

sulfate per liter, calculated as the anhydrous salt. The aluminum sulfate of commerce usually purchased by tanners contains about 18 percent of aluminum oxide and has a basicity of about 13 percent. Their stock liquor thus had the strength of a commercial aluminum sulfate solution of about 66 lbs. per 100 gals. For comparison, they also used a stock liquor of aluminum chloride. In each test they used 400 cc. of stock liquor, hide powder containing 2 grams of hide substance and caustic soda to raise the pH value to the desired value. The tests were carried out in widemouth bottles, which were shaken occasionally for 24 hours. The tanned hide powders were then washed free from soluble matter and analyzed for combined aluminum oxide. The results are shown in Fig. 244.

In the chart, "Grams Al_2O_3 Fixed per 100 Grams Collagen" means the same as "Lbs. Aluminum Oxide Fixed per 100 Lbs. Hide Substance." AlCl₃ means pure anhydrous aluminum chloride and $Al_2(SO_4)_3$ means pure anhydrous aluminum sulfate.

By referring back to Fig. 235 (p. 402), it will be noted from the curve for series No. 1 that a large fixation of chromic oxide occurs at pH values below 3.0 and that the pH value cannot be raised above 3.0 without causing precipitation unless salts are added. The pH value of the stock liquor of pure aluminum sulfate was 3.2 and practically no fixation of aluminum oxide takes place at that pH value. As the pH value is raised to about 3.8, the fixation of aluminum oxide increases sharply, but raising the pH value above 3.8 causes precipitation of aluminum oxide. In the procedure given above, the pH value can be raised to 4.2 because of the salts present.

Increasing concentrations of salts decrease the fixation of aluminum oxide at the same pH value just as it does the fixation of chromic oxide in chrome tanning. The writer carried out series of experiments in tanning with mixtures of aluminum sulfate and sodium formate, but obtained no results comparable with those obtained in chrome tanning upon the addition of sodium formate. Aluminum sulfate may form complexes with salts of organic acids, but apparently not with the vigor of formation of such complexes with chromic sulfate. Röhm patented the use of aluminum acetate or formate in the presence of the acetate or formate of an alkali or alkaline-earth metal, but the writer does not know to what extent this principle has been applied commercially.

Aluminum sulfate has been used for pretanning prior to chrome tanning and mixed with chromic salts during chrome tanning because it seems to make the leather somewhat tighter and smoother.

Aldehyde Tanning

Payne and Pullman patented the use of formaldehyde as a tanning agent in 1898. Leathers made by treating skins with formaldehyde are pure white and generally more resistant to the action of water than alum-tanned leathers. Formaldehyde has replaced alum to a large extent in the manufacture of furs and white, washable glove leathers. Formaldehyde has also been used for tanning sheepskins with the wool on, for white military leathers and as a pretanning agent for heavy, vegetable tanned leathers in order to speed up the penetration of the hides by vegetable tannins.

In practice, formaldehyde tanning is carried out in slightly alkaline solution. Bowes and Pleass studied the fixation of formaldehyde by purified hide substance and by purified goat hair as a function of pH value. In each test they added 1.6 grams of formaldehyde to 200 cc. of saturated limewater with the pH value adjusted to the desired value by the addition of hydrochloric acid. In each liquor

was placed 5 grams of purified hide substance (collagen) or 5 grams of hair. The tanning action was allowed to proceed for 48 hours and then the tanned collagen and tanned hair samples were analyzed for combined formaldehyde. Their graph showing the results is reproduced in Fig. 245.

Using caustic soda instead of saturated limewater gave essentially the same results. At pH values below 7.0, the fixation of formaldehyde by either the hide protein or the hair is relatively small, but with increasing pH value, the fixation increases rapidly. In tanning furs or skins with the hair on, it is interesting to note that the hair fixes even more formaldehyde than does the hide.

Some tanners have had the difficulty with formaldehyde tannage that leather having a grain surface that cracked rather easily was obtained. This weakening of the grain layer may be due at least partly to the swelling action that takes place in the absence of salt. The work of Theis and his co-workers shows the importance of having salt present to repress the swelling of the skins during tannage.

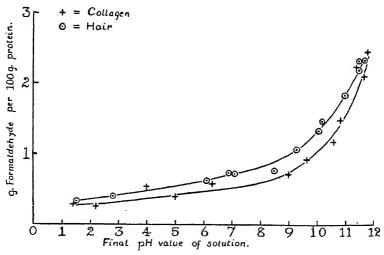


Fig. 245. Fixation of Formaldehyde by Hide Substance and by Goat Hair as a Function of pH Value.

They studied the effect of pH value in formaldehyde tanning in series of tests with goatskins run exactly as in their tests on Leukanol described above. As tan liquor, they used 1 percent solutions of formaldehyde, and the tanning time was 5 days. In this work, there were four series, two without the addition of salt, and two in which both the pretreating liquors of hydrochloric acid or caustic soda and the formaldehyde liquors were given 10 percent of salt on the weight of the liquors. The results are shown in Fig. 246.

The raw stock has its greatest resistance to heat in the range of pH values 5.0 to 8.0. The addition of salt to the raw stock greatly increases its resistance to heat. In fact, in the presence of salt, pH value has but little effect over the range 1.0 to 10.0.

If we may accept shrink temperature as a measure of degree of tannage, then it is clear that the addition of salt increases the degree of formaldehyde tannage and makes it nearly uniform over the pH range 5.0 to 10.0.

One procedure that the writer has found promising for calfskins, goatskins and sheepskins is first to pickle the stock as described in Chapter 9. Put a pack of 1000 lbs. pickled weight into a drum and add 80 lbs. of common salt in 100 gals. water at 70° F. Run 5 min. and start adding slowly, taking 1 hour to add, 30 lbs. of commercial formalin (this is 40 percent formaldehyde) and 10 lbs. of wood alcohol. Run 1 hour and start adding slowly, taking 1 hour to add, 10 lbs. of soda ash in 10 gals. water. Run drum for 1 hour after the last addition and let stand over night. Next morning measure the pH value and raise it very gradually by repeated additions of soda ash solutions until it reaches and remains at 7.5 for one hour. Then drain off the liquor and send the stock to be set out and shaved. After shaving, the stock is put into a fatliquor drum, washed in running water at 70° F. for 1 hour, and then fatliquored and dried.

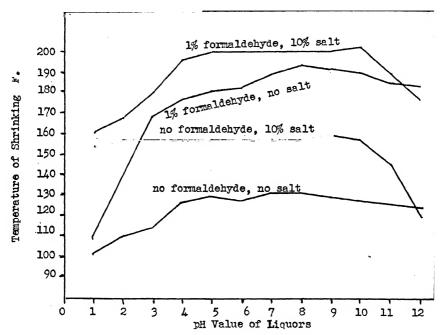


Fig. 246. Effect of Added Salt and pH Value of Liquors Used to Pretreat Goatskins and of Formaldehyde Liquors Used to Tan Them upon Their Shrink Temperatures.

Calgon Tanning

Calgon is the substance known to chemists as polymeric sodium metaphosphate. This material is a water-soluble glass developed as a water conditioner by Calgon, Inc. and Hall Laboratories, Inc. of Pittsburgh. When added to hard waters, it removes the lime and magnesium salts quantitatively and produces a water practically as soft as distilled water. When soap is dissolved in hard water, the lime present precipitates calcium soaps, which are greasy, waxy substances insoluble in water and the source of many annoying difficulties. When Calgon is dissolved in hard water and soap is added, not only are no calcium soaps formed, but any calcium soaps that may have been present are decomposed and the soluble sodium

soaps are regenerated. The name Calgon is a contraction of the words "Calcium Gone."

In 1935 the writer undertook research work for Calgon, Inc. to determine the possible uses for Calgon in the leather industry. In the course of this work, he discovered that Calgon has rather remarkable tanning properties.

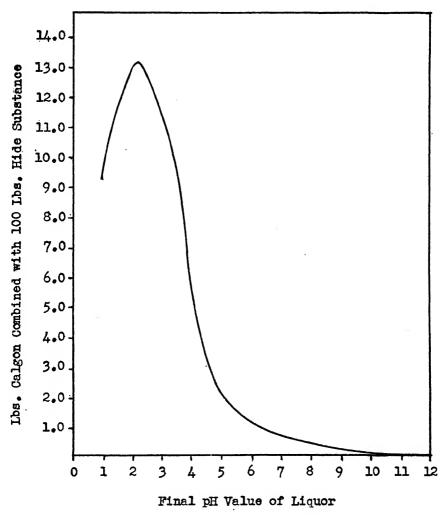


Fig. 247. Effect of pH Value on the Combination of Calgon with Hide Substance.

When raw hide is placed in an acid solution of Calgon, the Calgon penetrates it very rapidly and combines chemically with the hide substance, forming a pure white leather.

Like most tanning actions, the vigor of the combination is dependent upon pH value. In order to show quantitatively the extent of combination of Calgon with

hide substance as a function of pH value, the writer carried out a series of experiments with hide powder, the results of which are shown in Fig. 247.

Since this series of tests was run to determine the chemical equivalence of polymeric sodium metaphosphate and hide protein, commercial Calgon was not used. Dr. Everett P. Partridge, of Hall Laboratories, Inc., prepared for the writer the purest polymeric sodium metaphosphate that could be produced in the laboratory. This was really a chemically pure Calgon. The commercial Calgon Flakes used in tanning contains also some sodium triphosphate. The pure material contains 69.62 percent of phosphorus pentoxide (P_2O_5) and the Calgon Flakes 68.07 percent. A series of solutions was made with additions of sulfuric acid or caustic soda to produce final solutions containing P_2O_5 equivalent to 67.7 grams per liter. In each test 10 grams of air-dry hide powder was treated with 100 cc. of solution and shaken at intervals for 24 hours. The tanned powders were then placed in Wilson-Kern extractors and washed in running distilled water for 24 hours to remove all the uncombined metaphosphate. They were then analyzed for P_2O_5 and hide substance from which the parts of pure Calgon combined with 100 parts of hide substance were calculated to make the graph shown in Fig. 247.

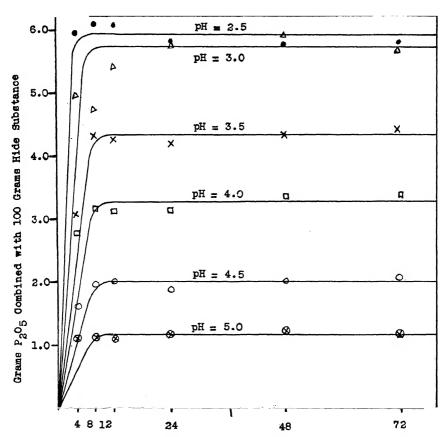


Fig. 248. Effect of Time and pH Value on the Fixation of Calgon by Bated Cowhide.

As increasing amounts of sulfuric acid are added to reduce the pH value to about 2.4, the Calgon combines with the protein in increasing proportions. As the pH value is reduced still further by the addition of more acid, the fixation decreases.

Fig. 248 shows the effect of tanning time and pH value on the tanning of bated cowhide with Calgon Flakes. The bated stock was put into drums and treated with 100 lbs. of Calgon Flakes in 108 gals. of water per 100 lbs. bated weight. This huge excess of both water and Calgon Flakes was used so that the removal of Calgon from the solution by the hide would have but little effect on its composition. In each test, the pH value was lowered to the desired value by adding sulfuric acid, and the pH value in each test was maintained throughout the tanning period. In each series, pieces of hide were taken out for analysis at the end of 4, 8, 12, 24, 48 and 72 hours. The ground samples for analysis were washed free from all soluble matter before analyzing for combined phosphate.

At a pH value of 2.5, where most Calgon tanning is done, equilibrium is established in less than 4 hours and no further increase in combination takes place with time, making it quite unlike other tanning materials in this respect.

In order to show the effect of the quantity of Calgon used, heavy cow hides were used. Bated stock was put into 6 drums and given a total volume of liquor of 10 gals. per 100 lbs. bated weight. The amounts of Calgon used per 100 lbs. bated weight were 1, 2, 4, 6, 8 and 10 lbs., respectively. The pH value of each liquor was reduced to 2.9 and was maintained at that value during a tanning time of 24 hours. The maximum fixation of Calgon occurred where the amount of Calgon Flakes used was 4 lbs. per 100 lbs. of bated weight; more Calgon than this did not bring about any greater fixation. The amount of P_2O_5 fixed by 100 lbs. of hide substance where 1 lb. of Calgon was used per 100 lbs. bated weight was 4.65 lbs.; where 2 lbs. of Calgon was used, it was 5.76 lbs. and where 4 lbs. of Calgon was used, it was 6.34 lbs.

There are a number of very valuable tanning substances that cannot be used alone to make commercial leathers, and Calgon appears to be one of them. In one comparative test, a calfskin was cut into sides along the line of the backbone, and one side was tanned with Calgon as the only tanning material and the other was put through the regular procedure for making chrome-tanned calf leather. When the Calgon-tanned side was washed before drying, it dried hard and tinny, even though none of the combined Calgon was removed. It was also found to absorb water much too readily to permit its use for shoe uppers. However, it was found to have some amazing properties. It was found to have the unprecedented tensile strength of 10,134 lbs. per square inch of cross-section as against only 3,212 lbs. for the opposite side tanned with chrome. Compared with the chrome side, the Calgon side had resistances to abrasion and to tearing more than three times those of the chrome side. When the leather was torn in a machine, the fibers showing along the torn edge were remarkably long and had a peculiar silky feel. resistance to abrasion was so great that the leather could not be buffed with Carborundum paper on a standard buffing machine. The leather was pure white.

Fig. 249 shows a vertical section of this leather magnified 140 diameters. The grain layer has become condensed to about one-third of the thickness of that of the side tanned with chrome. This explains the three-fold resistance to abrasion found. Similar comparisons with steer hides, goatskins and sheepskins showed the same relative differences between Calgon-tanned and chrome-tanned leathers.

Unlike the vegetable tannins and basic chromic sulfate, Calgon has not been used successfully as the only tanning substance for any kind of commercial leather. However, it has been found to be extremely useful in conjunction with other tan-

nages. The vegetable tanning of heavy stock is a notoriously slow procedure because the stock is hung into liquors in a vat, mechanical flexing being avoided as much as possible to keep the grain surface from becoming so rough and grainy as to preclude its general use. The writer has tried vegetable tanning bated stock in a drum with disastrous results. Vegetable tanning can be done in a drum after it has been penetrated by vegetable tannins in the rocker liquors, as described in Chapter 11. Large-scale tests have shown that vegetable tanning in the drum is about 46 times as rapid as vegetable tanning in the rocker vats and layers.

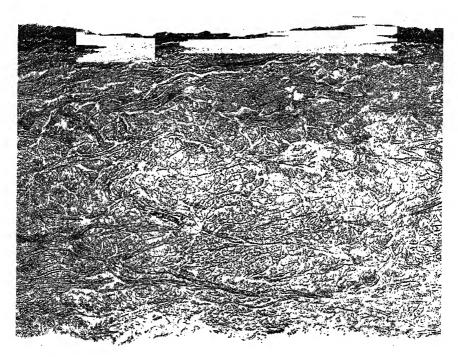


Fig. 249. Vertical Section of Calfskin Tanned with Calgon Alone.

Location: butt.

Thickness of section: 30 microns, or 0.00118 inch.

Magnification: 67 diameters.

Unlike vegetable tanning, chrome tanning is very rapid, not only because of the rapidity of penetration of the chromic salts into the hide, but very largely because it is done in drums. Chrome tanning can be done in drums because the drumming does not make the leather rough and grainy.

Calgon tanning can be done in a drum without any harmful effects, and the tannage is complete in a very short time. Calgon pretanned leather can be vegetable-retanned in a drum with no harmful effects; the vegetable tannins gradually displace the Calgon from combination with the hide. Thus by working the two tannages together, we get a very rapid vegetable tanning of stock in the drum without any harmful effects. For the past three years, vegetable-tanned leathers have been made in this way on a large scale with excellent results. The leather

retains some of the very desirable properties of the Calgon tannage and an improved tannage results.

Calgon-Vegetable Tanning

Any type of bated stock may be Calgon-tanned and then vegetable retanned, often to great advantage. The amounts of material required, however, increase with the thickness of the stock, not only because heavier stock contains less water and more hide substance, but also because stronger solutions penetrate thick hides more quickly. The general procedure will be described first for 40-lb. cowhides to be made into leather for bags, cases, golf grips, etc.

When vegetable tanning hides in a drum, care must be taken to avoid excessive mechanical action by using a drum about 7 feet in diameter and 7 feet wide and running at about 12 revolutions per minute. Put a pack of 1000 lbs. bated weight into such a drum, start drum running and add 50 lbs. of Calgon Flakes dissolved in 100 gals. of water. Run 20 min. and then add 18 lbs. of 66° Baumé sulfuric acid in 18 gals. of water, and run for 4 hours, when the pH value of the liquor should lie between 2.4 and 2.2. If the stock contains much lime, the pH value will be greater than 2.4, in which case add enough more diluted sulfuric acid to bring the pH value to 2.2. Always run the drum for an hour after adding acid. Then let stand over night. Next morning, if the pH value is less than 2.4, drain off the liquor and wash the stock in running water at 70° F. for 1 hour. If the pH value is greater than 2.4, add enough more acid to bring it to 2.2, run an hour, and then drain and wash.

Keep on hand a stock quebracho liquor made by dissolving 2300 lbs. of ordinary solid quebracho in 1000 gals. of boiling water, cooling, settling over night and decanting the clear liquor from the settled sludge. The final volume should be made to 1000 gals. at 70° F. To make the stock tanning liquor, add to the 1000 gals. of decanted quebracho liquor 300 lbs. of Leukanol. Cutch and spruce extracts may be used to replace some of the quebracho to increase leather yields and lower tanning materials cost.

After washing the stock, drain off the water and add 140 gals. of the stock tanning liquor. Run for 4 hours and pile the stock over night. Run the used liquor and the drainage from the stock to a storage tank for making up fresh stock tanning liquor. Next day press the stock and run the liquor from the press to the storage tank to be made up into new stock liquor. The pressed stock (about 50 percent water) is dry-milled for a minute to open it up and remove the creases, and is set out on a drum setting machine. It is then shaved, split to the required thickness and sent back to be retanned.

The procedure for calfskins and kipskins through the splitting and shaving is exactly the same as for the cowhides, except for the fact that only 30 lbs. of Calgon is required for calf and 40 lbs. for kip. After splitting and shaving, calfskins and kips are sent ahead for bleaching and retanning as described in Chapter 14.

The split cowhides are put back into the tanning drum and washed in running water at 70° F. and drained. Keep on hand also a dilute stock tanning liquor made by diluting each gallon of regular stock tanning liquor with 3 gals. of water. After the stock has been drained after washing, add 280 gals. of dilute stock tanning liquor, run for 3 hours and then haul out the stock and pile over night. Then bleach as described for calfskins in Chapter 14. Omit the retanning and send to be fatliquored. The used liquor and drainings are run to the storage tank to be strengthened as may be required from time to time to make new dilute stock tanning liquor.

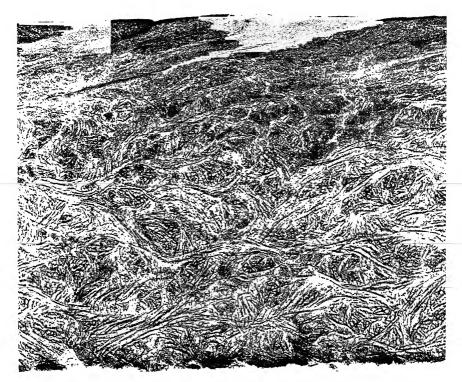


Fig. 250. Vertical Section of Calfskin Pretanned with Calgon and Then Retanned with Quebracho.

Location: butt.

Thickness of section: 30 microns, or 0.00118 inch. Magnification: 67 diameters.

It will be evident to the experienced tanner that the running time in vegetable tanning must never be less than that required for complete penetration of the stock by the vegetable tannins, and the thicker the stock the longer the drum will have to be run. The procedure as given is average for 40-lb cowhides to be split to produce leather of about 5- to 6-ounce weight.

For steer hides for sole leather, use 60 lbs. of Calgon to a 1000-lb. pack and run until it has completely penetrated the stock before washing. This can be observed by making cuttings from the thickest parts and examining the crosssections. The vegetable retaining is the same as for cowhides, but the amount of stock tanning liquor added may have to be increased considerably. The drum may have to be run for as long as 16 hours and must be run until the stock has been completely penetrated by tannin. After it has been completely penetrated, it is hauled out and piled on a truck for 48 hours. At this point, it is in a condition comparable with the sole leather described in the section entitled Rapid Tanning of Sole Leather in Chapter 11 (p. 337). Then proceed as described in the last paragraph of that section.

Fig. 250 shows a vertical section of calf leather Calgon-tanned and vegetableretanned as described above. After splitting and shaving, it was not bleached and retanned as described in Chapter 14, but was merely washed in running water at 100° F, for 20 min, and then fatliquored and colored as described in Chapter 15. It was then finished as described in Chapter 17. Although the tanning time was cut to a small fraction of that required without the use of Calgon, the properties of the finished leather were fully as good in every respect as that made by the much longer procedure. In fact, it was superior to the regular stock in strength and in resistance to abrasion. With Calgon tanning alone, these properties are increased threefold, but after vegetable retanning the gain averages only about 30 to 50 percent. By comparing Figs. 249 and 250, it will be noted that vegetable retanning opens up the highly condensed grain layer and changes the appearance of the fibers.

Calgon White Leathers

Leathers tanned with formaldehyde, then with Calgon and then with aluminum sulfate have been very satisfactory for shoe uppers, baseball covers and covers for white basketballs. This leather is usually made from calfskin, kipskins or light cowhides that have been split out of the limes. A typical procedure follows: Put 1000 lbs. bated weight into a drum and add 50 lbs. of common salt and 2½ lbs. of 66° Baumé sulfuric acid dissolved in 80 gals. of water at 70° F. Run 30 min.,

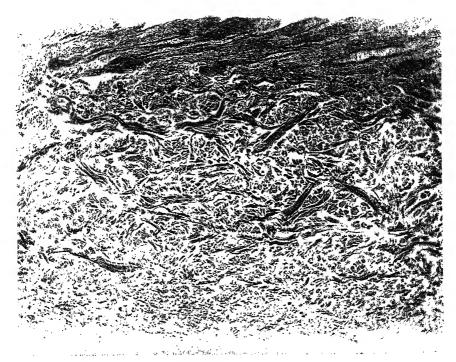


Fig. 251. Vertical Section of Calfskin Tanned Successively with Formaldehyde, Calgon and Aluminum Sulfate.

Location: butt.

Thickness of section: 20 microns, or 0.00079 inch.

Magnification: 67 diameters.

when the pH value of the liquor should be about 3.70, and add slowly, over a period of 30 min., 3 lbs. of soda ash in 3 gals. of water. Run 30 min. longer, when the pH value should be about 6.60, and drain. Wash in running water at 70° F. for 10 min., and drain.

Add 30 lbs. of 40 percent formaldehyde, 10 lbs. of wood alcohol and 20 lbs. of colloidal clay-A (Saxe-Rushworth Co.) in 80 gals. of water at 70° F. Run for 2 hours and then for 1 minute each hour during the night. Next morning the pH value should be about 6.50. Add 12½ lbs. of soda ash in 12½ gals. of water over a period of 1 hour and run for 1 hour longer, when the pH value should be about 7.50. Drain and wash in running water at 70° F. for 20 min., and drain. Add 50 lbs. of Calgon in 50 gals. of water at 70° F. Run 5 min. and add 30 lbs. of Tanoyl No. 1170X (National Oil Products Co.) and 20 lbs. of Tragasol (John P. Marston Co.) dissolved in 30 gals. of water at 70° F. Run 15 min. and add 15 lbs. of 66° Baumé sulfuric acid in 15 gals. of water slowly over a period of 1 hour. Run 2 hours longer, when the pH value should be about 2.60. Drain and wash in running water at 70° F. for 20 min., and drain.

Add 125 lbs. of aluminum sulfate, 50 lbs. of common salt, 20 lbs. of colloidal clay-A and 10 lbs. of Gardinol (Du Pont Co.) in 80 gals. of water at 70° F. Run for 4 hours and then for 1 min. each hour during the night, when the pH value should be about 2.30. Next morning add 30 lbs. of soda ash in 30 gals. of water slowly over an hour. Run 1 hour longer, when the pH value should be 4.20. Drain, haul out the stock, set out as smoothly as possible and hang to dry. The later operations are described in Chapter 17.

Tanoyl No. 1170X contains as essential ingredients both phosphorated and sulfonated coconut oils. Gardinol is produced by the sulfonation of higher fatty alcohols; it serves to produce a mellow feel in the leather. Tragasol has been discussed under Alum Tanning.

Fig. 251 shows a vertical section of calf leather tanned by the foregoing procedure. It was an excellent piece of pure white leather with a remarkable resistance to abrasion and of great strength. It made a fine piece of white shoe-upper leather. It required no finishing and was probably the purest full-grain white leather that the writer has ever seen.

Calgon-Chrome Tannages

No procedures will be given in this book for making leather with combinations of Calgon tanning and chrome tanning, because they have not been developed to the point of commercial use. However, they are extremely interesting and may some day be developed to the point of great commercial usefulness. If to a chrome liquor we add 1½ lbs. of Calgon for each pound of chromic oxide present, the chrome salts undergo a great change and are no longer precipitable by the addition of soda ash. If hides are tanned in this liquor, it will be found that the fixation of chrome increases with decreasing pH value, just the opposite of that found with chrome liquors without Calgon. Smaller additions of Calgon cause curious precipitations of complex metaphosphate-chromium compounds.

The uses of Calgon in fatliquoring and dyeing will be discussed in Chapter 15.

Oil Tanning

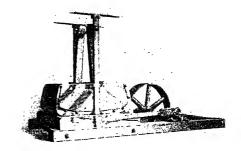
The tanning action of certain oils has been known and used since prehistoric times. Centuries ago skins of the Alpine chamois tanned with oil were in great demand for the clothing of gentlemen. As the true chamois became scarcer, tanners learned to prepare sheepskins for the leather that today is known as *chamois*. The process of oil tanning sheepskins is known as chamoising.

Sheepskins for chamoising are received in the pickled condition. Much of the raw stock is imported in casks holding about 1000 lbs. of stock each soaked in pickle liquor. A pack of 1000 lbs. pickled weight is put into a drum and washed in running water at 85° F. for 20 min., and drained. This removes much of the salt and the skins begin to swell because of the acid present. The skins are then placed in a hydraulic press and subjected to a pressure of about 200 tons. This presses out not only water, but a large amount of grease, which is sold to soap manufacturers. The pressed skins are dry-milled to open them up again, and are then fleshed very clean. The pack is then put into a drum and covered with water at 90° F. and run for 30 min., during which time they swell again and become quite plump.

Next, the stock is passed through a splitting machine, which separates the grain layer from the flesh layer. The grain layers are called sheep skivers and are tanned by methods already described for special purposes. The flesh layers are used to make the chamois leather of commerce.

In some tanneries, the whole pack of flesh layers is put into a drum without water and treated with 250 lbs. of cod oil. The drum is run for 4 hours, during which time the oil distributes itself through the stock and penetrates it to some extent. The stock is then piled and let stand for several hours, during which time fermentation of the oil begins to take place and heat is generated. After this, the skins are hung in a room where the air is kept damp and humid and left there for 2 or 3 days, while the oil penetrates the skins. Chemical reactions take place and some of the reaction products combine chemically with the hide protein. Acrylic aldehyde and other volatile and pungent products are also formed, and these escape into the room and are very irritating to the eyes, if sufficient ventilation is not provided.

Fig. 252.
Fulling Stocks.



Courtesy Turner Tanning Machinery Co.

After these chemical reactions in the skins are well under way (2 or 3 days), the skins are returned to the drum and the pack is treated with a second dose of 250 lbs. of cod oil, and the drum is run until the oil is taken up. The pack is returned to the humid room and kept hanging there for the chemical reactions to proceed until the stock is well tanned, usually 3 to 4 days.

Instead of drumming the skins with cod oil, some tanners put them into what are called *fulling stocks*, or *kickers* along with the oil. This machine was designed to soften hides and skins after soaking. It consists of two vertical arms, attached to a support above, which swing past each other when running. Attached to these arms are two cast-iron feet, made in the shape of steps, which pound and work the leather. A picture of the fulling stocks is shown in Fig. 252. The pummeling, or stocking, is stopped occasionally and the skins are spread out to cool. They are

oiled again and returned to the fulling stocks. The skins may receive several treatments with cod oil, or with seal, whale, shark or similar oils. Between the operations, the skins are piled up in heaps and covered with canvas. The chemical reactions that go on develop much heat, and it is necessary to turn the skins over occasionally to prevent damage from overheating. The duration of this tanning process is determined by the properties desired in the leather. The leather after tanning is drummed with water at 110° F., to which some soda ash has been added, and is then pressed to remove the bulk of uncombined oil; this is recovered and sold to tanners as a fatliquoring material under the name of moellon degras. The skins are then washed clean in running water.

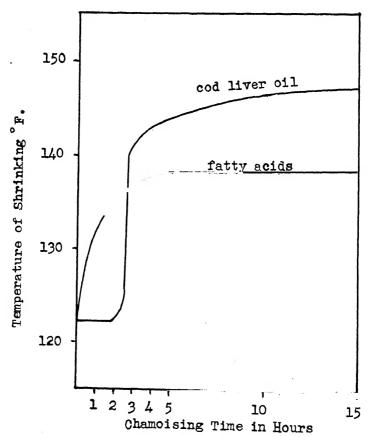


Fig. 253. Effect of Time of Chamoising Sheepskins on the Shrink Temperature of the Leather Produced.

The skins are then set out or wrung and buffed in the wet state, after which they are dried and spread out in strong sunlight to bleach.

Chambard and Michallet studied the effect of time on the chamoising action by measuring the shrink temperature of the leather at different intervals of tanning time. They coated the wet flesh splits of sheepskins with oil or with fatty acids and kept them in an enclosed chamber so that they would not dry out during the tanning action. At intervals, they withdrew pieces for determination of shrink temperature. They used olive oil, linseed oil, cod liver oil and the fatty acids of both linseed and cod liver oil. The olive oil had no measurable tanning action. Both the linseed oil and the cod liver oil tanned the skins very well, but the skins treated with cod liver oil were softer and finer. The fatty acids tanned the stock very quickly, but the resulting products were harsh.

The results for the cod liver oil and for its fatty acids are shown in Fig. 253. With the cod liver oil, there was no tanning action for 2 days, but on the third day the action was very rapid and the shrink temperature rose from 122 to 142° F. At the end of 15 days, the shrink temperature had risen further to 147° F. It was found that the skin had combined with 5.41 percent of its weight of oil. With the fatty acids, the tanning began at once and the shrink temperature rose in 1 day from 122 to 133° F., in 2 days to 135° F. and in 3 days to 138° F.; but after that there was no further increase in shrink temperature and the leather was harsh, and not soft and supple like that tanned with cod liver oil. After 15 days, it had combined with 7.77 percent by weight of the free fatty acids.

Chambard and Michallet then studied the effect of relative humidity in the chamber where the skins were hung during the tanning action. They found that relative humidity of the atmosphere of the chamber plays an important part in the tanning action. The results are shown in Table 42.

Table 42. Effect of Relative Humidity of the Atmosphere of the Chamoising Chamber on the Oil Tanning of Sheepskins.

Relative Humidity (%)	4 Days	k Temperature (°F.) 8 Days	after 15 Days	Combined Oil in Leather after 15 Days (%)
	(tann	age with cod live	er oil)	
0 20 40 70 100	115 118 122 118 118	118 118 126 120 118	127 127 142 145 149	4.32 5.41 5.46 7.05 7.30
	(tannage v	vith cod liver oil	fatty acids)	
0 20 40 70 100	131 131 131 131 131	133 138 138 144 145	131 136 136 145 147	7.09 7.35 9.05 8.95 9.10

It is quite apparent that moisture favors the chamoising action, the greatest degree of tanning, as shown by increase of shrink temperature, occurring after 15 days in atmospheres of 100 percent relative humidity. Again we find the initial action of the fatty acids greater than that of the oil itself, but the final action less, even though a greater amount of oil is taken up. In practice, the best results appear to be obtained from cod liver oil containing about 15 percent of free fatty acids.

Chambard and Michallet also showed that oxygen is necessary for the chamoising action. When the air of the chamoising chamber was replaced with nitrogen, no chamoising action took place. They also studied the effect of the pH value of the pickle liquor held by the stock, and obtained essentially the same results when the pH values lay between 1.5 and 2.0 as when neutralized to 7.0.

Tungsten Tanning

H. A. Herzog discovered that certain compounds of the metal tungsten have tanning properties. In his patent, he described a preferred method for their use, as follows:

"The skin or stock, such as cowhide, as it comes from the pickle, which may comprise 2½% of sulphuric acid and 6% of salt, will be given three washings in the wheel with 5% salt solution. This removes most of the uncombined sulphuric acid from the skins. The wheel is then drained and a solution of a tungsten compound is added. A satisfactory tungstate liquor has been found to be ten pounds of sodium tungstate for each one hundred pounds of stock or skins, the tungstate being dissolved in a suitable amount of water. 28% acetic acid is then added until the solution becomes acid, turning litmus red, and then sufficient salt to make a 5% solution.

"The wheel containing the skins and this tungstate solution or liquor is then run for three hours, at the end of which time an alum bath is added slowly and at intervals for one hour. A suitable alum bath consists of ten pounds of aluminum sulphate per one hundred pounds of stock or skins, dissolved in fifteen gallons of 5% sodium chloride solution. After the alum solution has been added the wheel is run for two hours longer, making three hours in all from the time the first portion of

the alum bath was added.

"The mixed solution is then drawn off and the skins thoroughly washed in the running water. They are now ready to be fat-liquored and subjected to the other usual steps or process to finish and prepare them for consumption.

"Instead of leaving the tungsten solution in the wheel and adding to it the alum solutions, it may be desirable or convenient first to withdraw the tungsten solution

before adding the alum.

"While preferably the skins are first subjected to the tungstate liquor for a substantial period of time, after which the alum bath is added, the process is not necessarily limited to this particular procedure or order but may be practised otherwise

within the scope of the appended claims.

"In practising the above described process it is essential that the hydrogen ion concentration (pH) be carefully controlled within fairly narrow limits if a true tanning is to be effected. It has been found that with a pH value of from 3 to 4 and again slightly below 8 the best results are secured, giving a leather with a tungsten content in the form of oxides of from 14 to 18% by weight, although a satisfactory leather may be obtained in which the tungsten content as calculated on the basis of the tungstic oxide is only a portion of these amounts.

"The process which is the subject of the present invention produces a leather which is permanently tanned by a tungsten compound; that is, tungsten in some form is combined with the fibres of the skin in such manner that no major portion of the tungsten will be lost upon washing. Where the tungsten compound, such as sodium tungstate, is used in combination with aluminum sulphate, as above described, the leather will have not only a surface of pleasing whiteness, but the same shade or color will be present throughout the body of the leather so that all cut and skived

edges have the same shade or color as the adjacent surfaces."

Early in 1937, the writer examined a white kip used for baseball covers that had been tanned with sodium tungstate. Per 100 lbs. of hide substance, it contained 15.82 lbs. of combined tungstic oxide and 2.26 lbs. of aluminum oxide. It was pure white throughout its thickness. It had a nominal tensile strength, but an unusually high tearing resistance and resistance to abrasion. It appeared to be a very satisfactory piece of leather. For a time it was made on a large scale, but the writer does not know of any tanner making it today.

Quinone Tanning

In 1908, Meunier and Seyewetz discovered the remarkable properties of benzoquinone, an organic substance that is very irritating to the eyes and not very soluble in water. From its water solutions, it combines very vigorously with hide protein and forms a leather resistant to the action of boiling water. The writer knows of no general use of quinone tanning nor of any established practice.

He tanned a bated calfskin by hanging it in a liquor kept saturated with quinone by using a great excess and stirring the solution from time to time. The pH value was kept at 6.10 and the skin was left in the liquor until a clipping showed that it would stand the boiling test (7 days). It was then washed, fatliquored, colored and finished as for chrome-tanned calf. 100 lbs. of hide substance combined with 12.6 lbs. of quinone. It had the unusually high tensile strength of 7,427 lbs. per square inch of cross-section and appeared generally to be a marketable piece of leather.

Although quinone is only slightly soluble in water, it is very soluble in alcohol. By using strong alcoholic solutions of quinone, the writer was able to tan calfskins in only a few hours, and the leather produced was very much like vegetable-tanned calf, but would stand the boiling test. Apparently the low water-solubility of quinone, its irritating properties and cost have been responsible for its failure to come into wide commercial use, because good leather can be made with it. Quinone tanning has great interest to the chemist in throwing light on theories of tanning; much information on the chemistry of quinone tanning can be obtained from the references given at the end of this chapter.

Miscellaneous Tannages

In this book on modern practice, an attempt has been made to give space to the various tanning materials in proportion to their commercial use by the industry. In the chemistry of tanning, many tanning materials that today are not important commercially in tanning may be very important in throwing light on the complex chemical reactions involved in tanning. Many materials that seem unimportant practically today may assume great importance in the future.

Since the eighteenth century, work has been done on the tanning of skins with salts of iron. This is well summarized in a book by Jettmar. Leather can be tanned with certain salts of iron, but the cheapness and availability of better tanning materials has been responsible for iron salts not coming into general

Leather can be tanned with sodium silicate and acid, but the leathers so obtained have not had all the desirable properties required in commercial leathers. The writer has done much work on the silicate tannages and believes that some day they may become very important, but it will require much more scientific work than has as yet been done on them.

The reference list given below contains much of little commercial importance today that may eventually become of very great importance.

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Chapter 14

Light Leathers from Tanning to Fatliquoring and Mold Control

When most leather comes from the tanning operation, it is very uneven in thickness and the flesh side may be very rough and contain some loose flesh. Since most leathers of commerce must be reasonably uniform in thickness and smooth on the flesh side, it is customary to level them by splitting and shaving before fatliquoring and dyeing. Since the hides tanned are sometimes much greater in thickness than is desired in the finished leather, they are split to reduce the thickness to the desired value. Sometimes, as in the manufacture of furniture leather, the hides tanned are so thick that they may be split into two or three layers, each of which may be prepared and finished for sale. In the case of some very light skins, splitting is unnecessary, and the skins are simply shaved to make the flesh side smooth and clean. For calfskins with butts much thicker than the shoulders, it is necessary to split only the butt areas to a thickness more nearly like that of the shoulders. After splitting, the skins are shaved to make the flesh side uniform and smooth.

For calfskins and heavier stock, the splitting and shaving operations can be done very much more efficiently if the water content of the stock is reduced from more than 70 percent, as it usually is after tanning, to about 50 percent. It is important also that the stock should be set out flat and smooth before splitting or shaving.

Pressing

One of the common methods of reducing the water content of the lighter vegetable-tanned leathers is pressing. The wet leather is folded into neat squares or rectangles and piled in a hydraulic press. The pressing of vegetable-tanned calfskins is shown in Fig. 173 of Chapter 11 (p. 315). After the pressure has been applied, liquor usually stops oozing from the pile when the water content has been reduced to a point between 50 and 55 percent. When the stock is taken from the press, it is very compact and sharply creased. Before splitting and shaving, it is necessary to open the skins and to remove the sharp creases.

This is very simply done in a few moments by an operation known as *wheeling*, or *milling*. For this purpose, a large, dry drum is used. A convenient number of pieces is put into the drum and it is run, allowing the pieces to tumble. In the course of a minute or two, the skins open and the creases gradually disappear. Upon coming from the drum, the stock may be split and shaved. For some heavier types of stock, where extreme smoothness is a requisite, it has been found desirable to set out the stock on a drum setting machine before splitting.

Wringing

For some types of stock, pressing is unnecessary; it is merely necessary to wring out as much water as can conveniently be done on one of the many types of wringers available. An old type of wringer still in use for stock to be split, as well as for sole and other heavy leathers not to be split, is the Quirin leather

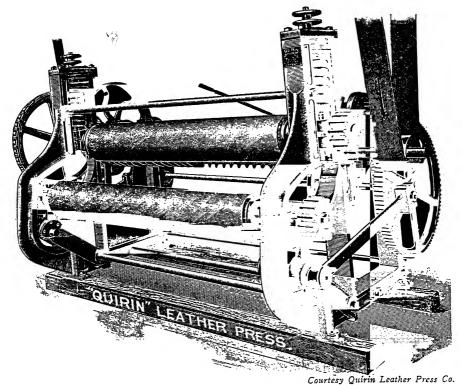


Fig. 254. Quirin Wringer.

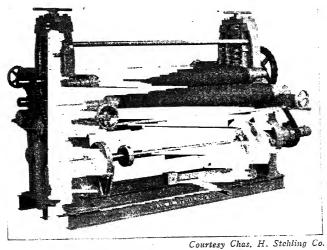


Fig. 255. Continuous-feed Wringing Machine.

press shown in Fig. 254. The two large rolls are wound with heavy felt. A hide or side is hung over the lower roll. Stepping on the treadle causes the two rolls to move together and grip the leather with great pressure. The leather is forced outward between the felt-covered rolls. At the same time a third roll.

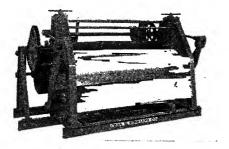


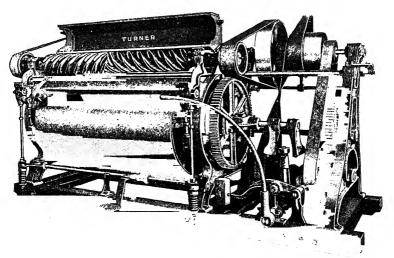
Fig. 256.

Combined Putting-out and Wringing Machine.

Courtesy Chas. H. Stehling Co.

equipped with blades, presses over the grain surface of the leather, and smooths it. In each operation, only a little more than half of the hide is wrung. It is then turned around and the other half is wrung.

Many modifications of the wringing machine have been developed having special features to improve special classes of stock. Fig. 255 shows a continuous-feed wringing machine that does not require any special experience to operate. It is designed for use on light, chrome-tanned leathers and for wool skins. After the stock has been put through this machine, it is dry enough to be split or shaved.



Courtesy Turner Tanning Machinery Co. Fig. 257. Drum Type Setting-out Machine.

Setting Out

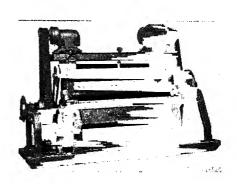
Another method of removing water from skins prior to splitting and shaving is called *setting out* or *putting out*. The fundamental principle is similar to that of wringing, but spiral blades set in a revolving cylinder smooth the leather and

extend its area. Fig. 256 shows a combined putting-out and wringing machine, which is suitable. It has the felt-covered rolls of the wringing machine and also the spiral-bladed cylinder of the putting-out machine, which smooths and extends the leather and eliminates pleats. It is used on both vegetable-tanned and chrometanned hides and skins.

A popular setting-out machine of the *drum* type is shown in Fig. 257. Below is a heavy, revolving bed that looks so much like a tanning drum when in operation that the machine is often referred to as a drum setting-out machine. The bed is built in the shape of a large cylinder, with a section of the cylinder removed. It is usually covered with a heavy rubber pad, acting as a bolster. The opening in the cylinder shows in the picture. One end of a hide or skin is put into this opening so that the rest of it lies with its area against the bolstered cylindrical bed. Upon pulling the lever, the cylinder starts to rotate, pushing the hide or skin against a revolving cylinder above, set with spiral blades. In the picture, the shielding cover is open so that the bladed cylinder may be seen. The bed makes

Fig. 258.

Leather Fleshing Machine.



Courtesy Chas. H. Stehling Co.

only about three-quarters of a revolution and then returns to the starting point. The pressure with which the leather is forced against the bladed cylinder can be varied to whatever extent may be necessary. The blades extend the area of the leather and smooth the grain surface, and the pressure developed squeezes out much of the water from the leather. This type of machine is used not only to remove water from leather preparatory to splitting and shaving, but also for making heavy leather smooth before hanging it to dry, as described in Chapter 18.

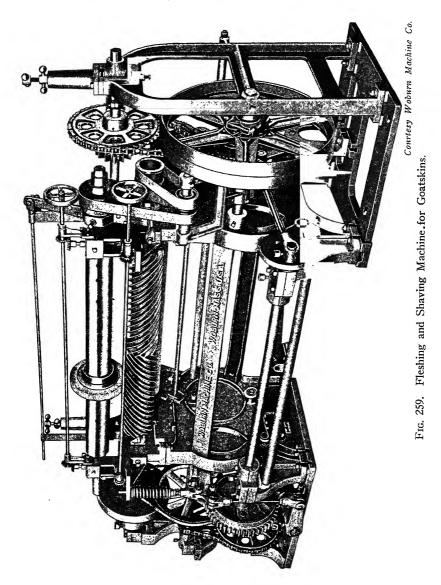
Some types of goatskins are not split at all and are not shaved in the ordinary way. After tanning, they are put through a setting-out machine that has attached to it a revolving cylinder set with spiral blades, which shave the flesh sides of the skins while they are being set out. Such a machine is shown in Fig. 258.

Another type of machine that both fleshes and shaves goatskins out of tan is shown in Fig. 259. The skins are handled on it directly from the tan liquors without any previous dewatering. The machine sets out, extends and smooths the skins as it shaves them. An emery wheel can be seen at the top of the machine. By throwing a clutch, while the machine is running, this wheel sharpens the blades of the cylinder.

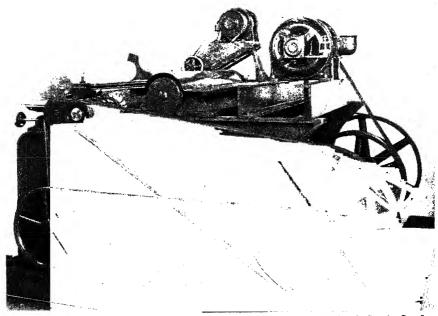
Fig. 260 shows the Wet Shaver made by the Fulton County Machine and Supply Co. for the wet shaving of glove leathers.

Fig. 261 shows a machine that does excellent work on wool skins. It not only removes the bulk of the water from them, but it sets them out, stretches and stakes them.

In Fig. 123 (p. 212) there is shown a serial-table unhairing machine. The skins are thrown over rubber-covered tables or boards and forced up between a pair of cylinders set with spiral blades. Machines built on a similar principle



are widely used for setting out calfskins after chrome tanning. In setting-out machines, it is common to have the skins pass between the blades in a more nearly horizontal direction. A battery of such setting-out machines in a calf tannery is shown in Fig. 262.

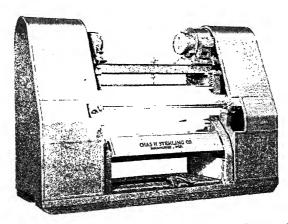


Courtesy Fulton County Machine & Supply Co., Inc.

Fig. 260. Wet Shaver.

Splitting

All leather to be split after pressing and wheeling or after wringing or setting out, is sent to the department of the tannery known as the *splitting room*, where there are batteries of both splitting and shaving machines. The modern splitting machine has a flexible knife in the form of an endless belt moving



Courtesy Chas. H. Stehling Co.

Fig. 261. Combination Putting-out, Stretching and Staking Machine for Wool Skins.

over a pair of large pulley wheels at high speed. Fig. 263 shows the Woburn whole-hide splitting machine. The pulleys over which the belt knife passes can be seen at either end of the machine. The path of the belt knife can be followed from one pulley to the other. The lower path of the knife shows as a black line under the bed of the machine. When the machine is running, any point on the knife passes from the top of one pulley across the bed of the machine to the other pulley and around it and under the bed of the machine back to the first pulley.

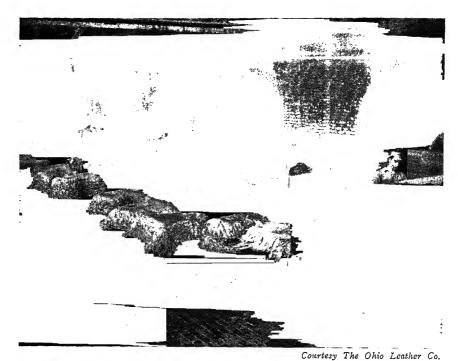


Fig. 262. Showing Chrome-tanned Calfskins Being Set Out by Machine in Large Calf Tannery.

When the leather to be split is placed on the bed of the machine and pushed forward, it is gripped by a pair of rollers and propelled forward in such manner that the belt knife cuts it into two layers. The propelling rollers are made up of a great many small ring rolls with rubber centers which allow for initial variations in thickness of the leather. The knife can be made to pass through the thickness of the leather at any desired depth below the grain surface by adjusting the level of the rollers with the levelling devices shown at the top of each end of the machine. These adjusters are equipped with micrometer gauges and can be set for any thickness of leather desired with great accuracy.

Each splitter is equipped with a micrometer hand gauge for measuring the thickness of leather. One type of gauge is shown in Fig. 264. It reads both in millimeters and in ounces. The ounce as a measure of thickness of leather originally meant the thickness required for 1 square foot of leather to weigh 1 avoirdupois ounce. This definition is unreliable as a measure of absolute thickness because

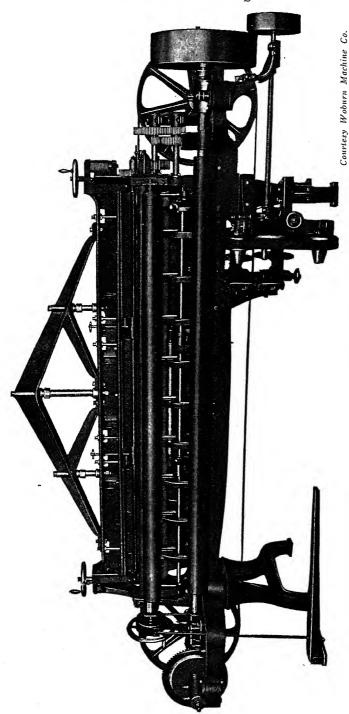
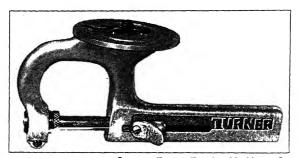


Fig. 263. Whole-hide Splitting Machine.

leathers of different kinds vary in their specific gravities. However, the ounce as a measure of thickness has come to mean & inch, or 0.39 millimeter. The Woburn gauge, also widely used, is shown in Fig. 379 of Chapter 17 (p. 579).



Courtesy Turner Tanning Machinery Co. Fig. 264. Leather Gauge.

The splitter first sets the adjusters at the points that have previously given him leather of the thickness desired. He then takes cuttings of the leather to be split and passes one through one end of the machine, another through the other end and one through the middle. He then makes adjustments until the pieces of the desired thickness come through at all points in the machine.

While the machine is running, the belt knife is automatically being sharpened. After the knife leaves the grinders, it passes through felt wipers before passing to the bed of the machine. These wipers remove the iron dust from grinding and should be cleaned or replaced at regular intervals to prevent the iron dust from getting on to the leather.

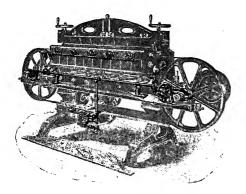


Fig. 265.

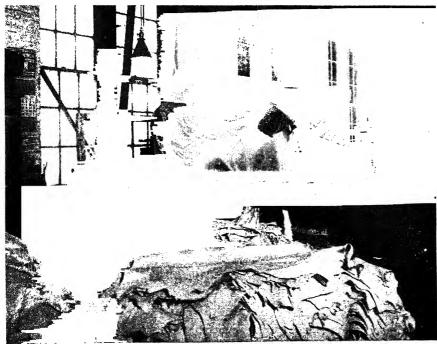
Splitting Machine Showing Chilson Attachment.

Courtesy Turner Tanning Machinery Co.

Although the splitting machine is simple in operation, it is rather complex in its construction, and different manufacturers have developed special features for their own machines that make for greater efficiency and simplicity of operation. In the Turner machine, the Chilson attachment has for its object the automatic regulation of the knife grinder and adjustment of the knife. By its use, much time is saved that is otherwise needed to adjust the machine. The resulting

adjust his machine in the morning and work practically continuously throughout the day without the annoyance of frequent shut-downs for adjustment. The automatic adjustment, compensating continuously for the wear on the knife and grinders, maintains the uniform bevel and position of the knife at all times, insuring uniform splitting without the aid of an expert operator. The Chilson attachment of a Turner machine is shown in Fig. 265.

Fig. 266 shows two operators at work on a splitting machine in the act of splitting chrome-tanned calfskins. The operator in the background is feeding the skins into the splitting machine and the operator in the foreground is taking them out and piling them. The flesh splits can be seen dropping out of the machine below the bed. Fig. 267 gives a little clearer view of the operator feeding a calfskin into the splitting machine; one pulley for the belt knife can be seen in the foreground.



Courtesy B. D. Eisendrath Tanning Co.

Fig. 266. Operators Splitting Chrome-tanned Calfskins.

Shaving

Fig. 268 shows a typical shaving machine. The shaving cylinder consists of spiral blades set in a revolving cylinder. The operator feeds the portion of a skin to be shaved between the bolstered backing roll and the shaving cylinder, with the flesh side toward the shaving cylinder. Upon stepping on the treadle, the skin is forced against the sharp revolving knife blades and moves forward until stopped. The same area can be fed into the machine repeatedly and its thickness is gradually reduced. Light skins that have not been split may be evened in thick-

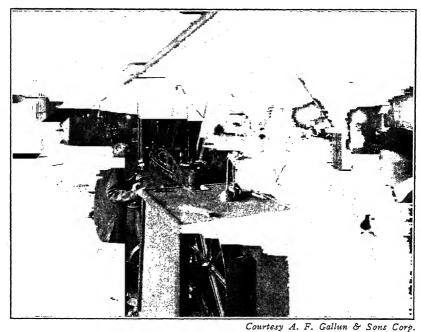
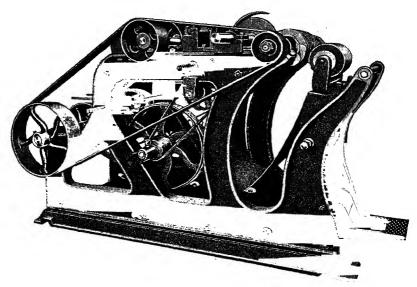


Fig. 267. Side View of Operators Splitting Vegetable-tanned Calfskins.



Courtesy Woburn Machine Co. Fig. 268. Shaving Machine.

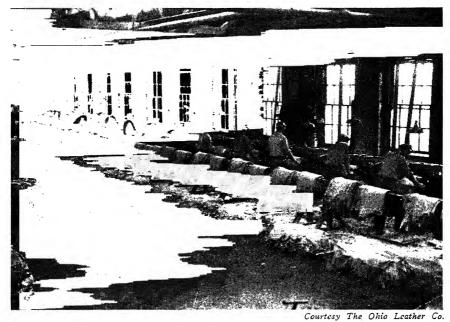


Fig. 269. Battery of Shaving Machines in Use in Large Calf Tannery.



Courtesy B. D. Eisendrath Tanning Co.

serve any useful purpose, washing immediately after tanning tends to prevent the

leather from becoming spotted.

If the leather has not been washed before splitting, put a pack of 1000 lbs. shaved weight in a drum and wash in running water at 80° F. for 1 hour. Where the stock has previously been washed, the stock is washed for only 5 min. After washing, drain off the wash water. Start the drum running again and add 12 lbs. of borax dissolved in 400 gals. of water at 80° F., taking 15 min. to add. Run 5 min. longer, drain, and wash stock in running water at 80° F. for 20 min. The stock is then ready for bottom dyeing, which will be described in Chapter 15.

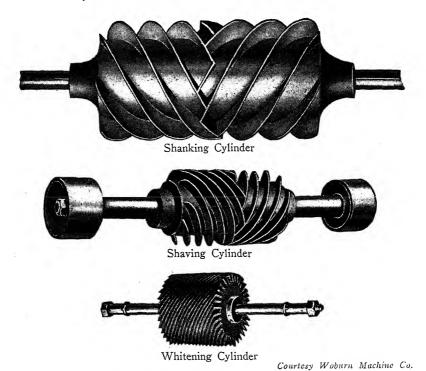


Fig. 273. Cylinders for Different Type Machines.

The amount of borax given is for calfskins chrome-tanned to a final pH value of 2.9. For other types of stock, the amount required may vary. This is only a surface neutralization to prepare the stock for the dyes.

Bleaching and Retanning Vegetable-tanned Calfskins

In the splitting room, vegetable-tanned leathers often become freckled with discolorations from the fine iron dust resulting from the continuous sharpening of the knife blades of the splitting and shaving machines. Such leathers may also contain insoluble matter from the tan liquors imbedded in the grain surface. There is an old method of bleaching such stock with borax and sulfuric acid that removes imbedded insoluble matter from the grain and lightens and brightens the color of the leather; this is still much in use for many types of vegetable-tanned leathers. A common method of bleaching follows:

Put a pack of 750 lbs. shaved weight into a drum and wash in running water at 80° F. for 20 min. and drain. Add 5 lbs. of borax in 40 gals. of water at 100° F., run 15 min., and drain. Then wash in running water at 100° F. for 20 min., and drain. Then add 5 lbs. of 66° Baumé sulfuric acid in 40 gals. of water at 100° F., run 5 min. and drain. Then wash in running water at 100° F. for 20 min. and dump the pack.

The stock is then retained as follows: Make up a stock retaining liquor by dissolving 1000 lbs. of ordinary solid quebracho extract in 1000 gals. of boiling water, allowing to cool and settle and pumping off the clear liquor from the settled sludge, which is discarded. The liquor will have a barkometer reading of about 38°. Run 2000 gals. of water at 70° F. into a 2500-gal. paddle vat and add enough stock retaining liquor to give the liquor in the paddle a barkometer reading of 3°. Then dump into the paddle vat 1500 lbs. shaved weight of stock from the bleach, or 2 drum lots. Run the paddle for 5 min. and again for 5 min. each hour during the working day, and for 5 min. three times during the night. The stock is left in the liquor for 3 days, and each day the paddle is run for 5 min. out of each hour and for 5 min. three times during the night. The tannin content of the liquor is maintained at about 0.7 percent by adding stock retanning liquor each day. Each liquor is used for about 25 successive packs of stock. As the liquor is used repeatedly, it requires a higher barkometer reading to maintain a tannin strength of 0.7 percent. For the first pack, strengthen the liquor each day to $3\frac{1}{2}^{\circ}$ barkometer; the second pack to 4° barkometer; the third to $4\frac{1}{2}^{\circ}$, the fourth to 5°, and all succeeding packs to 5½° barkometer. At the end of three days in the liquor, haul out the pack and send to be fatliquored as described in Chapter 15. After using a liquor for 25 successive packs, run it to the sewer and make up fresh liquor. The acid carried into the liquor from the bleach tends to maintain the pH value of the liquor at about 3.4.

For stock tanned in the stick vats and rockers, as described in Chapter 11, the operations of bleaching and retanning are essential to make good leather. The bleaching clears the grain and brightens the color of the leather and the retanning gives the leather plumpness and body; it also overcomes spotting caused during splitting and shaving, and safeguards against undertannage in the yards. Although the retan liquors are weak, they add much to the combined tannin, raising it from about 37 lbs. to more than 50 lbs. per 100 lbs. of hide substance. The use of weak liquors also conditions the stock better for fatliquoring. If the stock, when fatliquored, contains too much water-soluble matter, it does not take the fatliquor properly, and the grain surface is likely to dry hard, cracky, and of uneven color. If the stock does not contain enough water-soluble material, it takes up the fatliquor very greedily and the stock is likely to become too soft and raggy because the fatliquor penetrates too deeply into the stock.

When Calgon-pretanned stock has been vegetable tanned in a drum for only a few hours, as described in Chapter 13, the fixation of tannin is usually great enough to make retanning unnecessary, and the low pH value of the liquors so brightens the color of the stock as to make bleaching unnecessary unless the stock has been discolored in the splitting room. When retanning is omitted, the stock must be washed more before fatliquoring, to avoid having too great a content of water-soluble matter in the leather.

For Calgon-pretanned, vegetable-retanned cowhides for bag, case and golf-grip leather, follow the bleaching procedure given above for calfskins, and send to be fatliquored without retanning.

Permanganate Bleach

Sheepskins for chamois leather are often brightened in color by bleaching with potassium permanganate. This bleach is also often given to any raw stock to be tanned for white leather. The principle of this bleach will be illustrated by a procedure for a pack of 1000 lbs. of bated calfskins to be tanned for white leather. Put pack into drum, start the drum running, and add 75 lbs. of common salt and 10 lbs. of 66° Baumé sulfuric acid in 100 gals. of water at 60° F. Run 10 min. and add 5 lbs. of potassium permanganate in 30 gals. of water at 60° F. Run 20 min. and add 7½ lbs. of anhydrous sodium bisulfite in 20 gals. of water at 60° F. Run 30 min.; the stock should then appear pure white and the pH value of the liquor should be about 4.0. Add 6 lbs. of soda ash in 15 gals. of water at 60° F. and run 1 hour; the pH value should then lie between 6 and 7. Wash in running water at 60° F. for 30 min. and send stock ahead for the white tannage.

Mold Growths

The subject of mold growth might well have been treated at any point in this book because molds abound everywhere in the tannery. However, molds rarely cause the tanner much trouble until after the stock has been pickled or tanned. He frequently applies fungicides in pickling or after tanning, usually during the fatliquoring or finishing operations for light leathers, in the oil wheel for sole leathers, or in the stuffing drum for harness leathers. In vegetable tanning heavy leathers, the liquors usually become heavily contaminated with molds; but tanners rarely attempt to destroy them there because the microörganisms on which they depend for acid production would also be destroyed.

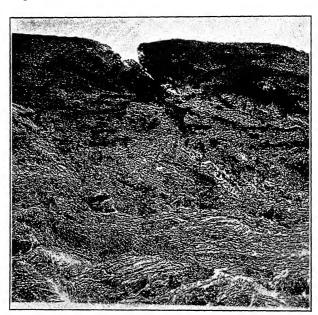


Fig. 274. Vertical Section of Vegetable-tanned Calf Leather Showing Mold Spot.

Location: butt.
Thickness of section: 30 microns, or 0.00118 inch.



Fig. 275. Vertical Section of Vegetable-tanned Calf Leather Showing Mold Growing Among Fibers.

Location: butt.

Thickness of section: 30 microns, or 0.00118 inch.

Magnification: 250 diameters.

Foodstuffs, cloth, leather, and most of the organic materials of our everyday life become covered with a growth of mold when left exposed to damp air for several days. The ease with which mold spores are blown about makes their appearance in the atmosphere of common occurrence. In the tan yard, liquors which have not been agitated for two or three days are usually covered with a soft, velvety carpet of molds of various colors. Leather kept in a damp condition is almost sure to become covered with mold in the course of a few days. Mold is a source of considerable annoyance to tanners because it produces spots on leather which cannot be removed by any practical means known at present without damaging the leather itself. Since preventive measures must be used to guard the leather against mold damage, it is highly desirable that those who handle leather much should know something about the life and habits of molds as well as how to keep them from spotting the leather.

The danger of bacterial damage is greatest before the skin has been tanned, but mold spots may appear on shoes or leather in any other form at any time after it has been dampened. These spots are not uncommon and appear as varied in size, shape and distribution as freckles on the human face. When leather has been dampened and contaminated with spores from the atmosphere or from the watery solution used, it is likely to develop spots after damping again at any later date. After the first damping, the molds begin to grow, but they may not have time to develop into visible spots before the leather is dried again. With each subsequent wetting, an opportunity is afforded for further growth until the spots become pronounced.

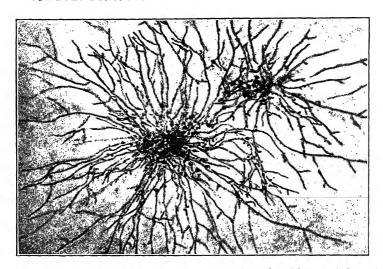


Fig. 276. Aspergillus Niger from Spotted Leather after 16 Hours' Growth.

Magnification: 37 diameters.

Wilson and Daub made a detailed study of spots produced on leather by molds. Fig. 274 shows a section of vegetable-tanned calf leather cut through the center of a black, freckle-like spot, one of thousands which covered the skin. The skin itself is not attacked, but the spot is due to the presence of a black mold. Fig. 275 shows a portion of the same spot at higher magnification so that individual cells may be seen. The spots resisted every kind of chemical treatment tried which did not harm the leather. However, in a test piece the spots disappeared when the



Fig. 277. Aspergillus Niger from Spotted Leather after 40 Hours' Growth.

Magnification: 37 diameters.

leather was kept under ideal conditions for mold growth for a month; it was then completely covered with a heavy layer of mold, but when this was brushed off, the spots were gone. The procedure was interesting, but hardly practical.

Molds present a more complex structure than bacteria or yeasts, being multicellular and having a more complicated method of reproduction. The molds consist of two kinds of cells, assimilative and reproductive. In their growth, they form a

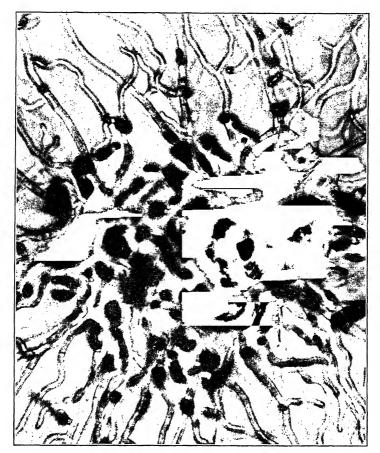


Fig. 278. Aspergillus Niger from Spotted Leather after 16 Hours' Growth.

Magnification: 280 diameters.

cobweb-like mass of branching threads from the surface of which tiny fertile threads project into the air bearing the part of the plant from which the spores develop. The main mass of branching threads is called the *mycelium* and an individual thread a *hypha*. The species of mold is generally told by the nature of the spore-bearing or fertile hypha. In most molds the mycelium is *septate*; that is, the hyphæ are divided by cross walls, called *septa*.

The Buchanans list five general families of common molds: (1) Mucoraceae, whose spores are frequently borne in a spore case, called a sporangium, and whose

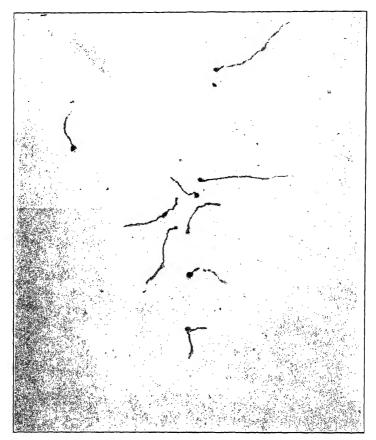


Fig. 279. Aspergillus Niger Spores 24 Hours after Inoculation.

Magnification: 50 diameters.

mycelia are often nonseptate. (2) Mucedinaceae, whose spores, called conidia, are never borne in a sporangium, whose mycelium is septate, whose fertile hyphae or conidiophores are not united into definite bodies, and whose hyphae are not dark or smoky. (3) Dematiaceae, like Family 2 except for the fact that either or both the hyphae and conidia appear dark. (4) Stilbaceae, whose conidiophores are united into stalks or bundles. (5) Tuberculariaceae, whose conidiophores are united into a definite layer or stratum.

Since it is possible here to give only a brief description of molds and their behavior on leather, it seems best to follow Wilson and Daub in their study of Aspergillus niger, isolated from spotted leather.

Aspergillus niger belongs to the family Mucedinaceae and is differentiated from other members of the family by having the following characteristics: Its conidia are one-celled and are borne in chains and its conidiophores are sharply differentiated from the mycelium and inflated at the apex. The conidiophores are unbranched and usually relatively long. At the swollen apex there are numerous short stalks, called sterigmata, usually set close together, giving the conidiophore

the appearance of a war club with spikes. These sterigmata are relatively short, practically always branched, and from their tips the chains of spores are differentiated.

Preparation of Cultures for Study

Wilson and Daub obtained their cultures for study from leather showing black spots. The surface of each strip of leather was first passed back and forth quickly through a flame. The strip was then suspended from a cork in a bottle over water protected against continuous contamination from the outside air. In the course of about a week each strip was covered with a miniature forest of black mold which had grown out from the interior of the leather. Innumerable tiny threads projected out from the leather, each supporting a ball of black spores.

By means of a platinum loop, some of these spores were transferred to tubes of Bacto potato-dextrose agar and incubated at 98.6° F. Fresh cultures were made from time to time by inoculating new tubes with spores from the older ones

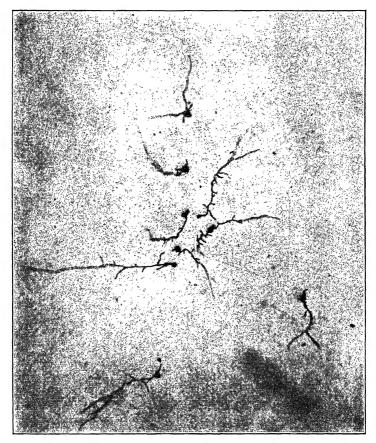


Fig. 280. Aspergillus Niger Spores 26 Hours after Inoculation.

Magnification: 50 diameters.

and the purity of each culture was assured by making platings and comparing the individual colonies.

For study under the microscope, glass slides were fitted with culture chambers, into each of which was put about 5 drops of the agar medium. A few spores were transferred from a culture tube to 10 cubic centimeters of Bacto beef broth liquor and shaken well and then a tiny quantity of this liquor was

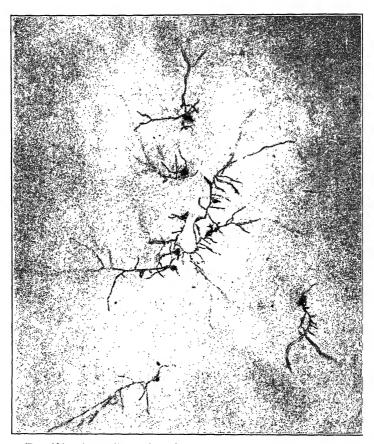


Fig. 281. Aspergillus Niger Spores 28 Hours after Inoculation.

Magnification: 50 diameters.

transferred to the center of the culture chamber by means of a needle. The culture chamber was sealed from the air by means of a removable cover glass. All of the customary precautions were taken to prevent contamination of the cultures being studied. At intervals during their growth, the cultures in the glass culture chambers were photographed for permanent record.

For details of the best modern methods for studying molds, the reader is referred to the book of Thom and Church.

Fig. 276 is a photomicrograph of the mold in one of these chambers which was kept in an incubator at 98.6° F. for 16 hours after inoculating. Fig. 277

shows the same old mold after 40 hours at 98.6° F. Fig. 278 is the same as Fig. 276 except for the higher magnification. Here the septa in the mycelium are plainly visible.

Nature of Growth

The development of spores is illustrated in Figs. 276 and 277. From the branching mycelium shown in Fig. 276, fertile hyphae have developed upward

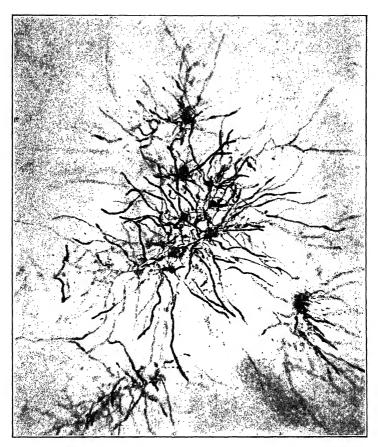


Fig. 282. Aspergillus Niger Spores 32½ Hours after Inoculation.

Magnification: 50 diameters.

and fruited with the formation of spherical spore masses shown in Fig. 277, each such mass having a diameter of about 0.15 millimeter and each individual spore a diameter of about 0.004 millimeter.

Figs. 279 to 283, inclusive, illustrate the growth of the mold from individual conidia or spores. Culture slides were inoculated and watched, under the microscope. The need for keeping the slide under the microscope at all times prevented incubation at the optimum temperature for the growth of this mold, which is

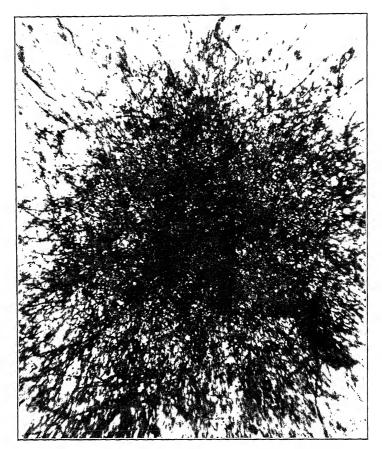


Fig. 283. Aspergillus Niger Spores 48 Hours after Inoculation.

Magnification: 50 diameters.

from 91° F. to 99° F. Since the temperature averaged about 77° F., the cultures did not grow nearly so rapidly as that shown in Figs. 276 to 278.

Fig. 279 shows nine spores 24 hours after inoculation. They have already sent out little branches, the beginning of the formation of their mycelium. The further development during the next few hours is pictured in Figs. 280 to 283. Actually one can project the mold onto the ground glass of the camera and watch it grow. At the end of 48 hours, the picture has changed to that shown in Fig. 283; on the surface of leather, this would have been a black spot about two millimeters in diameter.

When the mold is allowed to spread out freely on a culture plate, the fruiting stalks, or conidiophores, arrange themselves in rhythmic, concentric circles. The center of a Petri dish containing potato-dextrose agar was inoculated as in the case of the culture chamber containing the spores shown in Fig. 279. The dish was kept in the incubator at 98.6° F. for six days, when the colony had grown to a diameter of about five centimeters. It is pictured at low magnification in

Fig. 284 and a portion of it at higher magnification in Fig. 285. The mycelium does not show because the focusing was done on the spore heads.

Industrial Importance

Aspergillus niger is important commercially in the fermentation of sugars to gallic and citric acids. Under anaërobic conditions, it will convert sugars into alcohol. It secretes, under favorable conditions, a great variety of enzymes, of which Thom and Church list the following: lipase, amylase, inulase, raffinase, gentianase, zymase, melezitase, invertase, maltase, trehalase, cellobiase, emulsin, urease, protease, nuclease, rennet, and the enzyme tannase, which has been blamed for losses of tannin in the tan yard. This formidable list of enzymes would indicate that it is not safe to let Aspergillus niger run wild in the tannery.

Thom and Church examined tan liquor from a fermenting vat and found the predominating mold to be Aspergillus niger, with minor admixtures of a species of Penicillium (Citromyces) and yeast. Van Tieghem's identification and

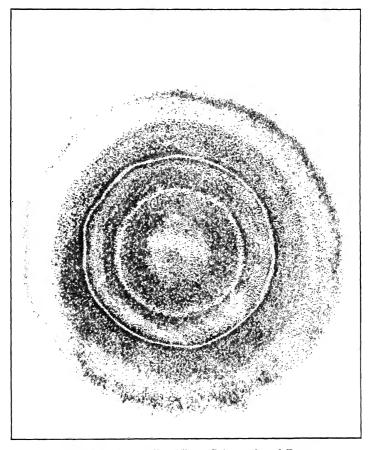


Fig. 284. Aspergillus Niger Colony after 6 Days. Magnification: 1.8 diameters.

description of Aspergillus niger resulted from his study of fermenting tan liquors and form the beginning of our real knowledge of the biochemic importance of the Aspergilli. Knudson found a progressive increase in tannase with the addition of tannin in Czapek's solution with 10 percent sugar, with Aspergillus niger as the fermenting agent. Maximum production of tannase occurred when 2 percent tannic acid had replaced all of the sugar in the formula.

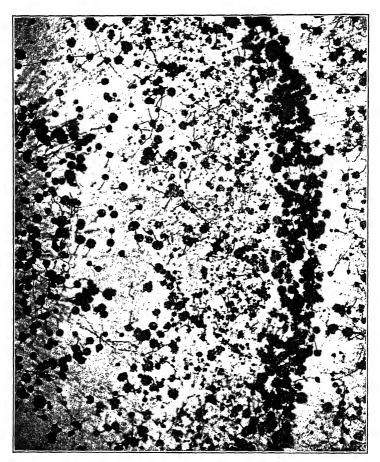


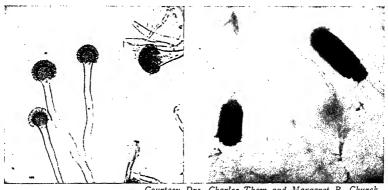
Fig. 285. Aspergillus Niger Colony after 6 Days.

Magnification: 14 diameters.

Aspergillus niger thrives in acid solution and grows particularly well on chrome leather. The author has observed this mold growing vigorously on chrome calf leather, which was neither fatliquored nor colored, when immersed in any strength of pure sulfuric acid solution up to and including 0.4 lb. per gal. It did not grow in acid solutions of 0.53 lb. per gal. or stronger. Its growth was quickly stopped by immersion in dilute caustic soda solution, indicating that an alkaline medium is not favorable to its development.

Other Molds

Thousands of species of molds have been described, but the great majority of those found in the tannery belong to the two groups: Aspergilli, and Penicillia. Wilson and Daub isolated 12 species of mold from a single strip of leather, which were identified as follows by Drs. Charles Thom and Margaret B. Church, of



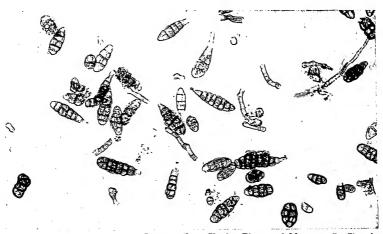
Courtesy Drs. Charles Thom and Margaret B. Church.

Fig. 286. Heads of Aspergillus Fumigatus.

Fig. 287. Heads of Aspergillus Terreus.

Magnification: 260 diameters. Magnification: 260 diameters.

the Bureau of Chemistry, United States Department of Agriculture: Five were species of Aspergillus; five were species of Penicillium; one was a species of Macrosporium (or Alternaria); and one a species of Brachysporium. The species of Aspergillus were niger, flavus, fumigatus, terreus, and nidulans. Two of the species of Penicillium belonged to the group known as divaricatum (Thom:



Courtesy Drs. Charles Thom and Margaret B. Church.

Fig. 288. Spores of Macrosporium or Alternaria.

Magnification: 260 diameters.

Paecilomyces varioti Bainier). Both Penicillium and Aspergillus belong to the family Mucedinaceae.

The Macrosporium and Brachysporium belong to the family Dematiaceae. In this same family is the species Dendryphium, whose conidia grow in chains. In a study never carried far enough to justify publication, Wilson and Daub isolated a species of Dendryphium from spotted leather and made a few preliminary tests which indicated that this species of Dendryphium was even more to be feared than Aspergillus niger in the spotting of leather.

Fig. 286 shows the heads of Aspergillus fumigatus, Fig. 287 the heads of Aspergillus terreus, and Fig. 288 the spores from a species of Macrosporium. These are published through the courtesy of Drs. Charles Thom and Margaret B. Church.

It is easy to distinguish *Penicillium* from *Aspergillus* by the manner in which the spore-bearing structures are borne. In *Penicillium*, the conidiophores branch in whorls, giving rise to a terminal cluster of parallel threads, of which each ultimate branchlet is to be regarded as a sterigma. From each of these a chain of conidia is developed. The branches and conidia together resemble a broom or brush. The name *Penicillium* is Latin for little brush. Several hundred species of both *Aspergillus* and *Penicillium* are known.

Prevention of Mold Growths

Mold growths on leather need not be feared so long as the leather is kept dry because molds require water for their growth and development. However, it is sometimes necessary in the tannery to keep leather in the wet state for a sufficient time to permit mold growth. In such cases, mold growth can be prevented by the proper use of fungicides. If pickled stock is to be kept for a long time before tanning, fungicides can be added directly to the pickle liquor; this is sometimes done in the case of pickled sheepskins. If chrome-tanned stock is to be kept damp for a long time before fatliquoring and dyeing, it is desirable to add fungicides to the chrome liquor before hauling out the stock. In damp and humid weather, many tanners add fungicides to the fatliquor or stuffing material. Wherever mold growths are found on leather in the tannery, it is desirable to add fungicides to liquors used on the leather just prior to the point in the procedure where the mold growth was discovered.

Of the common fungicides studied by Wilson and Daub, the most effective against Aspergillus niger was an aqueous solution of chlorine. One part by weight of chlorine in 50,000 parts of water killed the mycelium and fruiting portions of the mold in 10 minutes. Many tanners are not equipped to use chlorine, but there are many substances conveniently handled that are very effective in killing molds. Collatone (Lehn & Fink), known chemically as para-chlormeta-cresol, is a convenient white powder that is about one-fourth as effective as free chlorine per unit weight. Mercuric chloride is only about one-fifth as effective as Collatone.

Two of the very common fungicides often used in fatliquoring leather are beta-naphthol and sodium pentachlorphenate (Dowicide-G) of Dow Chemical Co., and Santobrite of Monsanto Chemical Co. Beta-naphthol is not very soluble in water, but can be made to dissolve very readily by adding 4 oz. of caustic soda to each 1 lb. of beta-naphthol. The writer has found that mold growth can be prevented or greatly retarded in wet leather after fatliquoring by adding to the fatliquor 1 lb. of beta-naphthol per 1000 lbs. of wet stock to be fatliquored.

There is a also a whole series of Dowicides available that are very effective,

but they differ in price and fungicidal value. In practice, the tanner can quickly learn the minimum amount of any fungicide required to keep his leather free from mold growth.

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Chapter 15

Fatliquoring, Stuffing and Dyeing Light Leathers

After leather has been tanned, it generally dries hard and stiff unless oils and greases are incorporated into it. The oils and greases give the leather softness, fullness, mellowness and flexibility and greatly add to its strength and ability to stretch without cracking. Centuries ago, the application of oils and greases to leather consisted chiefly of smearing the oils and greases over the surfaces of the wet leather and allowing it to dry. If the leather was dry at the time of the application, it remained greasy and dark in color. When the oils and greases were applied to the wet leather, it was light in color when dry, with little sign of greasiness when the operation was intelligently done

There is an old saying that oil and water do not mix, meaning that most oils are not soluble in water. However, if a drop of oil is placed in water, it usually floats and then begins to *spread* over the surface of the water. If a can of oil is dumped into a pond, the oil will spread over the water until the entire surface of the pond is covered with oil, even though the thickness of the layer of oil is so thin that it cannot be measured. This property of spreading over water surfaces is common to most oils that are not soluble in water and it is very important to the tanner to become familiar with it. If leather is pressed to remove the water between the fibers, leaving the fibers themselves still wet, and oil is applied to the surface of the leather, the oil begins to spread over all water surfaces, which causes it to penetrate into the leather and spread over the surfaces of all of the fibers. This uniform distribution of the oil is responsible for the light color and lack of greasiness of the leather.

If the leather is soaking wet and the water in its interior is continuous with the water on its surface, the oil does not penetrate because it spreads only over water *surfaces*.

On the other hand, if the leather is dry at the time of application of the oil, there is no spreading, and the oil remains in the leather surfaces, making it dark in color and greasy.

Following this method of applying oils and greases to leather, the operation known as *stuffing* was developed. In this operation, the leather is freed from all surplus water, usually by pressing, and the stock is tumbled in a drum with the molten or liquid oils and greases, which penetrate into the leather by spreading over the wet fibers. The leather must be wet, but great care must be taken to avoid the presence of so much water that the oils will not penetrate.

The operation of fatliquoring originated in the twentieth century. Large amounts of water are used, and the oils are applied in the form of oil-in-water emulsions. Although oils are generally insoluble in water, many soaps are very soluble. If soap is dissolved in water and oil is added and the mixture is agitated violently enough to break the oil up into fine globules, the oil then does not separate from the water upon standing. The soap coats the surface of each tiny globule of oil and provides it with a sort of pseudo-solubility. The oil is not truly dissolved in the water, but the tiny globules remain suspended in the water,

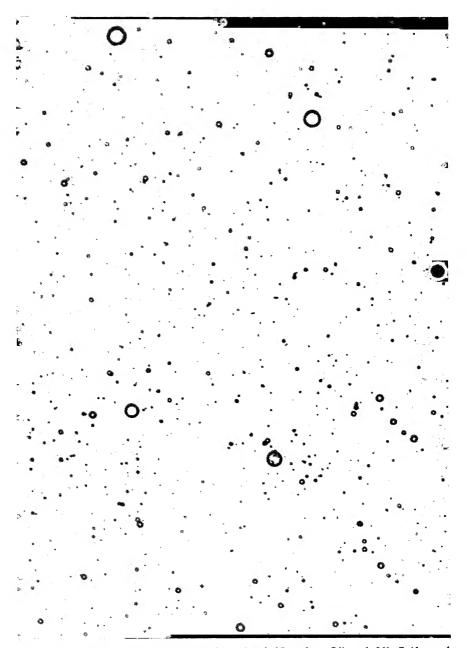


Fig. 289. Photomicrograph of Emulsion of 2% Neatsfoot Oil and 3% Sulfonated Neatsfoot Oil in 95% Water.

Magnification: 412 diameters.

with little or no tendency to coalesce and separate from it. The mixture remains as a stable emulsion.

When certain oils are treated with concentrated sulfuric acid, chemical reactions take place in which sulfo fatty acids are formed. When these are neutralized, soaps are formed, which have important emulsifying actions upon neutral oils.

A typical fatliquor emulsion can be made by mixing 2 lbs. of neatsfoot oil with 3 lbs. of sulfonated neatsfoot oil and pouring it slowly and with stirring into 95 lbs. of very hot water. The emulsion appears milky white to the eye and the oil does not readily separate from the water. Such an emulsion is shown in Fig. 289 at a magnification of 412 diameters. In order to get this picture, a drop of the emulsion was placed on a microscope slide and covered with a cover glass. The slide was then placed in a microscope and photographed by means of a special illuminating system known as dark-field illumination. The water appears as a black background and the oil as brilliantly illuminated globules suspended in it. There are a few relatively large globules present, but most of them are very tiny. The largest globule shown in the picture has a diameter of only about 0.001 inch. Many of the globules have diameters less than 0.00001 inch.

When wet leather is drummed with such an emulsion, these tiny globules of oil penetrate into the leather and combine with it. Since the even distribution of the oil in the leather does not depend primarily upon the spreading properties of the oils, as in stuffing, large amounts of water can be used.

There are a great many different kinds of oils used in fatliquoring leather, and their choice for any type of leather depends not only upon the characteristics desired in the leather, but also upon price, availability and adaptability to any specific procedure for making leather. In the fatliquoring procedures described in this chapter, particular fatliquors will be described which are known to give satisfactory results in large-scale operations. They may not be the best fatliquors for the purpose and many others might be used equally well.

Fatliquoring Vegetable-tanned Light Leathers

The following procedure is suitable for vegetable-tanned calfskins taken after bleaching and retanning, as described in Chapter 14, for Calgon-vegetable tanned calfskins after tanning, as described in Chapter 13, for bag and case leathers and for practically any other type of vegetable-tanned leathers not exceeding 7 oz. in weight. Many such vegetable-tanned leathers are first given the bleaching operation described in Chapter 14.

Put a pack of 750 lbs. shaved weight into a drum, fill the drum to the gudgeon with water at 100° F., run 10 min., and drain. Wash in running water at 100° F. for 10 min., and drain. Then add 37½ lbs. of Tanoyl No. 1170 (National Oil Products Co.) in 50 gals. of water at 120° F., run 20 min., and measure the pH value of the liquor. If it is above 3.8, add dilute sulfuric acid very cautiously with the drum running until the pH value of the liquor is reduced to 3.6. Usually this will require only about 8 oz. of 66° Baumé sulfuric acid. In uniform, routine operation, the amount to be added is known in advance and can be added without stopping the drum and waiting for the pH determination. Run the drum for 5 min. after adding the acid; then haul out and pile the stock. This small addition of acid has the effect of causing the leather to take up practically all the fatliquor from the solution. Allow the stock to remain in a pile over night and then hang up each skin head down to dry.

In fatliquoring leather, each square foot of leather takes up practically the same amount of oil. In the case of calfskins, the leather may vary greatly in thick-

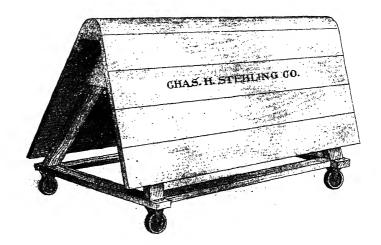
ness. If the pack of skins contained some leather of 2-oz. weight and some of 4-oz. weight, the leather of 4-oz. weight would receive only one-half as much oil by weight as the 2-oz. leather, because each receives the same amount per square foot. In the case of leather split completely to uniform thickness, the amount of oil received by weight is much more uniform.



Fig. 290. Fatliquored Vegetable-tanned Calfskins in Dry Loft Awaiting Selection for Coloring.

In the case of calfskins or other leather having varying thicknesses, after drying the skins are examined for softness. As a rule, the thicker skins will be much harder than the thinner ones, and so the entire pack must be assorted according to softness. Those soft enough are simply sent to the loft to be kept until ordered out for coloring. The harder skins are accumulated into new packs and fatliquored a second time, following the procedure given above, except for using only one-half as much fatliquor.

Unlike chrome-tanned leather, vegetable-tanned leather can be dried out and then wet back again very readily. This is one reason why vegetable-tanned leathers are fatliquored before coloring. If they do not get enough fatliquor in the first operation, they can be wet back and refatliquored, and this can be repeated until they have just the amount that is most desirable. Then they can be stored indefinitely in the dry condition and dyed only after the order for any particular color has been received. A dry loft showing vegetable-tanned calfskins awaiting selection for coloring is shown in Fig. 290.



Courtesy Chas. H. Stehling Co. Fig. 291. Wooden Horse with Sloping Sides for Piling Leather.



Courtesy B. D. Eisendrath Tanning Co.

Fig. 292. Calfskins after Dyeing, Fatliquoring and Horsing for Draining.

Fatliquoring and Dyeing Black Chrome-tanned Leathers for Dress-shoe Uppers

This procedure can be used for calfskins, kipskins or split cowhides; in fact, it can be used for any chrome-tanned leathers of thickness suitable for shoe uppers. The stock is taken after the regular chrome tanning (not the formate tanning), as described in Chapter 12, and after splitting, shaving and neutralizing, as described in Chapter 14. It is necessary to know both the *shaved weight* of the pack and its *total area*. When there is any serious doubt as to the approximate area of a pack, it is a simple matter to measure it on the machine to be described in Chapter 17. Most tanners simply estimate the area from past experience.



Courtesy B. D. Eisendrath Tanning Co.

Fig. 293. Setting Out Calfskins after Dyeing and Fatliquoring.

In Chapter 14, a procedure was given for washing and neutralizing a pack of 1000 lbs. shaved weight. After final washing, drain off the water. Knowing the approximate area of the pack, add the following quantities of materials per 100 square feet of leather in the drum: Start drum running and add 4 gals. of water at 120° F. Then add slowly, over a period of 10 min., 5½ oz. of Direct Black dye in 4 gals. of water at 120° F. Run 5 min. longer and drain. Then add 2½ oz. of Hematine and 0.7 fl. oz. of concentrated ammonia in 4 gals. of water at 120° F., run 15 min. and drain.

Then for the entire 1000 lbs. shaved weight of stock in the drum add 80 gals. of water at 120° F. and run 5 min. Then add 15 lbs. of Tanoyl No. 1170 (National Oil Products Co.) in 50 gals. of water at 120° F. and run 20 min. Then measure

the pH value of the liquor; if it is above 3.8, add enough dilute sulfuric acid with the drum running to lower it to 3.6, and run for 5 min. after the last addition of acid. Then haul out the stock and pile it on wooden horses to drain for several hours, or over night. In order to minimize wrinkling, it is customary to use wooden horses with sloping sides, like that shown in Fig. 291. Fig. 292 shows calfskins taken from the drum after dyeing and fatliquoring, and horsed for draining.

After draining, the stock is set out as smoothly as possible before drying. For calfskins, in order to make them very smooth, this is often done in three separate operations: machine setting, machine shanking and hand setting. After the stock on the horses has drained sufficiently, it is moved to the setting-out machines. Fig. 293 shows a setting-out machine in operation on calfskins. The

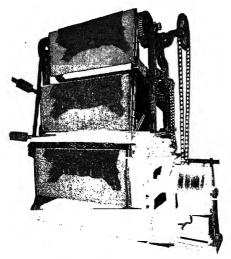


Fig. 294.

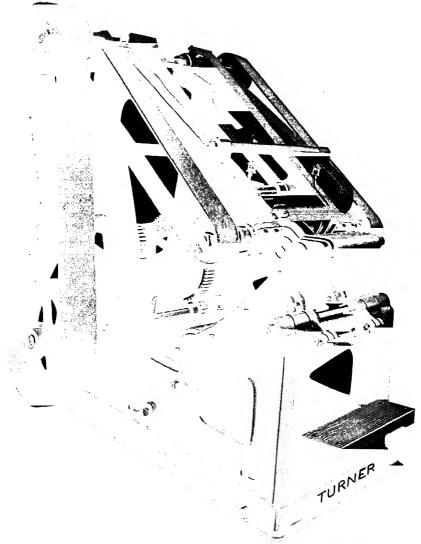
Serial-table Putting-out Machine.

Courtesy Turner Tanning Machinery Co.

operator places a skin over a moving table bolstered with heavy sheet rubber. The table moves forward between a pair of spirally bladed revolving rollers, which set out the skin on both sides of the table. The skin is taken off from the other side of the machine and the empty table returns under the machine to receive another skin. In passing through only one pair of bladed rollers, the part of the skin along the edge of the table does not get set out. When single-table machines are used, the skins are usually taken off the end of one machine and placed on another, with the wet strip so placed that it gets properly set out on the second machine.

To overcome the disadvantage of having to put each skin through two machines or twice through the same machine, a serial-table type of machine has come into wide use. Fig. 294 shows a vertical machine of the serial-table type that has proved very satisfactory. It consists of a series of bolstered tables moving in a Ferris-wheel type of motion, like the unhairing machine shown in Fig. 122 of Chapter 8. When an empty table appears before the operator, he places a skin on it, with the backbone line along the edge of the table, which then moves up and between a pair of rollers set with spiral blades, which set out the skin. After passing through the first set of revolving blades, the bolster on the table shifts so that

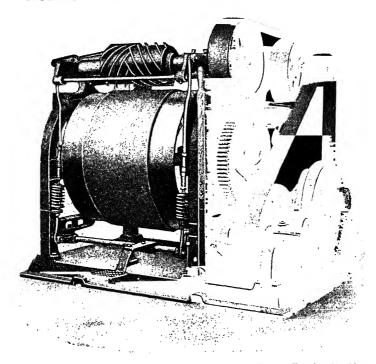
when passing between a second set of revolving blades, the backbone line of the skin, missed on the first passage, also gets set out properly.



Courtesy Turner Tanning Machinery Co.

Fig. 295. Shank Setting Machine.

In setting out leather after coloring, it is necessary not only to remove as much water as possible, but also to get the grain surface as smooth as possible before drying. The shanks of calfskins have a tendency to become drawn when tumbled wet in a drum, and they require a special setting operation to make



Courtesy Turner Tanning Machinery Co.
Frg. 296. Turner 36-inch No. 3 Drum Setting Machine.

them very smooth. Fig. 295 shows a machine especially designed for this purpose. When each of the four shanks of a calfskin is fed into the machine separately, a specially designed, bladed roller spreads them out, extends their areas and makes them very smooth. The special arrangement of blades in the cylinder of a shanking machine is shown in Fig. 272 of Chapter 14.

Fig. 296 shows a setting machine designed for setting out pieces, bellies, heads, flanks and odd pieces of offal leather. It has been widely used by manufacturers of strips of leather for shoe counters. The cut shows the machine equipped with a cylinder with a working length of 24 inches, but cylinders are obtainable of any length from 20 to 36 inches.



Fig. 297. Hand Slicker.

Courtesy Chas. H. Stchling Co.

For fine types of leather, the requirements for smoothness of grain surface are so great that the leather is finally set out by hand after the heavy work of setting has been done by machine. This operation is called *hand slicking*. It is usually done with the type of *hand slicker* shown in Fig. 297.

It consists of a rectangular blade of steel or brass set in a wooden handle.

Usually the skin, previously worked out as smoothly as possible by machine, is laid out flat on a sloping marble table, grain side down, and the *slickers* press on the leather with the blades of their hand slickers with considerable pressure and push forward as shown in Fig. 298. Fig. 299 shows this operation from a different angle and in more detail. The slickers try to smooth out any sign of wrinkle or graininess in the skins and trim off any loose or straggly ends. When they work on the flesh side of a skin, the operation is called *setting on the flesh*. When they turn the skins over to smooth out any irregularities in the grain surface itself, the operation is called *setting on the grain*. The job of the slicker is a very import-

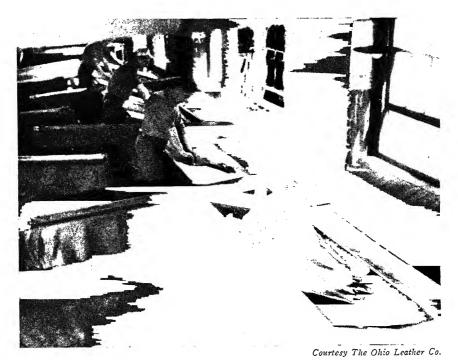


Fig. 298. Hand Slickers at Work Setting Out Calfskins before Drying.

ant one because any fine wrinkles left in the leather at this stage become permanent upon drying, and the value of the leather is greatly lowered. When working on the grain side of the skins, he must be sure that his blade contains no nicks to scratch the leather, and he must at all times keep his blade in good condition for most efficient setting out of the stock.

After the leather has been set out by hand, it is handled with extreme care until after it has been dried. Details of the methods of drying leather will be described in Chapter 16.

Fatliquoring and Dyeing Colored Chrome-tanned Leathers for Dress-shoe Uppers

In the following procedure, only the classes of dyes will be indicated, because it is obvious that the specific colors and shades that can be produced in leather



Courtesy B. D. Eisendrath Tanning Co.

Fig. 299. Detailed View of Hand Setting a Calfskin.

are enormous and the colors used change with styles and popular demands. As in the case of making black leathers, we shall start with 1000 lbs. shaved weight of stock in the drum after neutralizing, washing and draining.

Per 100 square feet of leather in the drum, add 4 gals. of water at 130° F., run 5 min. and then add slowly, over a period of 10 min., 4 oz. of a mixture of acid dyes of the desired color in 4 gals. of water at 130° F. Run 15 min. longer and add 5 oz. cube gambier dissolved in 2 gals. of water at 130° F. Run 20 min. and drain. Then add 2 oz. of tartar emetic in 4 gals. of water at 70° F., run 5 min., and drain. Wash in running water at 100° F. for 10 min., and drain.

For the entire lot of 1000 lbs. shaved weight add 50 gals. of water at 105° F., run 1 minute and add 40 lbs. of egg yolk, 15 lbs. of sulfonated neatsfoot oil and 5 lbs. of borax in 30 gals. of water at 100° F. Run 30 min. and drain.

Per 100 square feet of leather, add 20 oz. of ground Sicilian sumac leaves in 2 gals. of water at 110° F. Run 30 min. and add 2 oz. of soda ash in 2 gals. of water at 70° F. Run 5 min. and drain. Wash in running water at 70° F. for 5 min. and drain. Add 5 oz. of aluminum sulfate in 2 gals. of water at 70° F., run 5 min., drain and wash in running water for 1 min. and drain. Then add slowly, over a period of 10 min., 2 oz. of basic dyes of desired color in 4 gals. of water at 110° F. Run 10 min. longer and drain. Then add 4 gals. of water at 70° F., run 1 min. and haul out the stock. Pile on wooden horses and set out as described for black leather.

The amounts of dyes given are only approximate; deeper shades require cor-

respondingly more dye. An enormous variety of fatliquors may be used, each giving the leather definite characteristics. In this book, it was considered sufficient to describe one fatliquor for blacks and another for colors known to be used on a large scale and to give very satisfactory results.

Dyeing Vegetable-tanned Leathers for Shoe Uppers

This leather has already been fatliquored and dried. As the amounts of materials to be used are based entirely upon area, the pack is made up to have a total area of 2000 square feet. Put the whole pack of dry leather into a drum, cover with water and then wash in running water at 75° F. for 5 min., and drain. Then add 25 lbs. of ground Sicilian sumac leaves in 25 gals. of water at 110° F., run 30 min. and add 50 fl. oz. of 90 percent formic acid in 50 gals. of water at 80° F., run 10 min., and drain. Wash in running water at 70° F. for 10 min., and drain. Add 3 lbs. of tartar emetic in 25 gals. of water at 70° F., run 5 min., and drain. Wash in running water at 70° F. for 10 min., and drain. Add 6 lbs. of aluminum sulfate in 25 gals. of water at 70° F., run 5 min., and drain. Then wash in running water at 70° F. for 10 min., and drain.

Dissolve basic dyes of the desired colors (25 to 150 oz., according to depth of color desired) in 100 gals. of water at 120° F. Make quite sure that the dyes are completely dissolved before adding to the drum. It is best to have the dye solution in a reservoir tank with brass piping leading to the hollow gudgeon of the



Courtesy A. F. Gallun & Sons Corp.

Fig. 300. Tacking Vegetable-tanned Calf Leather on Wooden Frames to Dry After Dyeing, Setting-out and Oiling-off the Grain.

drum and a valve to control the rate of flow into the drum. Add 100 gals. of water to the drum and start the drum running. Then allow the dye solution to flow into the drum at such rate that it takes just 15 min. for it all to flow in. Run 5 min. longer, and drain. Add 100 gals. of water at 110° F., run 1 min., drain and horse the stock. Then set out as described for black chrome upper leather.

In making black vegetable-tanned leathers, use 7 lbs. of the basic dye Janus

Black in 100 gals. of water at 120° F., but omit the tartar emetic.

After setting out vegetable-tanned calf leathers, coat the grain surface with a mixture of 3 parts denatured olive oil to 1 part light paraffin oil and tack out to dry on wooden frames, as shown in Fig. 300.

Dyeing and Fatliquoring Stock Chrome-tanned in Presence of Sodium Formate

In Chapter 12 a method was described for increasing the fullness and plumpness of chrome-tanned leathers by increasing the amount of chrome liquor used and adding sodium formate to it. Leathers tanned in this way are so much plumper than leathers tanned without the addition of sodium formate that they require more fat-liquor to give them the desired degree of softness. They also acquire a deeper shade of green from the chrome. Dyes also penetrate into such leathers to a greater depth, making it necessary to use more dye to get the desired color. The same methods of dyeing and fatliquoring as those described above may be used, but it is desirable to double the amount of fatliquor used and it will be found necessary to increase the amounts of dyes used.

Elk Leathers

Elk leathers are generally made from cowhides, but they are split to a heavier weight than for dress-shoe upper leathers. They are often used for work shoes and sport shoes. Because they are heavier leathers, it is desirable to make them softer for comfort. This can be done by chrome tanning them to a greater degree at higher pH value and by incorporating more fatliquor into them. If ordinary methods of chrome tanning have been used, it is customary to retan the leather in chrome liquor after splitting and shaving.

For stock tanned in the regular way, as described in Chapter 12, take the stock after splitting and shaving and make up into lots of 800 lbs. shaved weight each. Put a pack of 800 lbs. shaved weight into a drum and wash in running water at 70° F. for 30 min., and drain. Add 100 gals. of water at 80° F., run 1 min., and add slowly over 1 hour 10 gals. of stock sulfur-dioxide chrome liquor, described in Chapter 12, which contains the reaction products of 2 lbs. of sodium dichromate per gal. Run the drum for 4 hours after all the stock chrome liquor has been added, and let stand over night. Next morning, start the drum running and add slowly over a period of 1 hour 15 lbs. of hypo dissolved in 50 gals. of water at 80° F. Run 20 min. longer, and drain. Wash in running water at 70° F. for 30 min. and then in running water at 120° F. for 10 min., and drain.

Add 100 gals. of water at 120° F., run 1 min. and add 9 lbs. of Fustic crystals and $7\frac{1}{2}$ lbs. of Hypernic crystals dissolved in 50 gals. of water at 120° F. Run 20 min. and drain. Then add 100 gals. of water at 120° F., run 1 min. and add slowly over 10 min. 6 lbs. of Resorcine Brown dissolved in 25 gals. of water at 120° F. Run 10 min. longer, and then add the Elk fatliquor described below:

Dissolve 8 lbs. of *Castile soap* in 25 gals. of boiling water in a 50-gal. wooden barrel. Mix 8 lbs. of *flour* to a paste with water and add to the boiling soap solution. Then add 5 lbs. of *Irish moss* dissolved in 5 gals. of boiling water. Then

add 10 lbs. of carnauba wax emulsified, as described below, in 10 gals. of water. Continue to boil while adding 20 lbs. of waterless moellon and 45 lbs. of sulfonated cod oil. Cool to 125° F., add 1 pint of concentrated ammonia, mix well and add to the running drum. Run 30 min. and drain. Add 100 gals. of water at 70° F., run 5 min., drain, haul out the stock, pile and let stand over night.

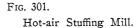
To make the 10 gals. of carnauba wax emulsion, mix 1 lb. of oleic acid and 7½ oz. of triethanolamine (Carbide & Carbon Chemicals Corp.) with 9 gals. of water, and heat to boiling. Melt 10 lbs. of carnauba wax by heating to 190° F., but do not allow the temperature to go higher than this. Pour the molten wax slowly and with vigorous stirring into the water solution. Then add the whole mixture to the fatliquor.

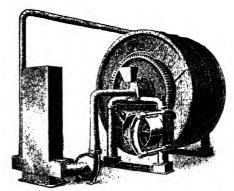
Set out the stock as smoothly as possible, and send to be dried.

The procedure as given is for a common tan shade of elk leather. For black elk, use $9\frac{1}{2}$ lbs. of *Hypernic crystals* and 6 oz. of *copperas* instead of the *Fustic* and *Hypernic*, and use 10 lbs. of Direct Black instead of the Resorcine Brown. For other colors, simply use dyes of the desired shades from the list of *direct dyes* available. [See pages 511-15.]

Dyeing and Stuffing Waterproof Chrome-retanned Upper Leathers

The chrome retanning of this stock after splitting and shaving has already been described in Chapter 13. The stock is taken after pressing and wheeling. It is made up into packs of 600 lbs. pressed weight. For *natural color*, the color imparted to the leather by retanning with vegetable tanning materials is sufficient and no





Courtesy Turner Tanning Machinery Co.

dyes are used. For blacks, it is sufficient to lay the sides, grain side up, onto a table and brush the grain surface evenly with a solution of 3 oz. of Direct Black and 2 fl. oz. of concentrated ammonia per gallon of water. For various colors, it is best to apply the dyes in a drum in order to get uniform coloring. Put a pack of 1000 square feet of leather into a drum and wash in running water at 120° F. for 20 min., and drain. Add 50 gals. of water at 120° F., run 1 min. and add 1 lb. of Congo Red, 1 lb. of Acid Orange and 1 lb. of Direct Green in 50 gals. of water at 120° F. for a chocolate shade. For other colors, simply use the dyes required to give the desired shade. Run 30. min., haul out the stock and set it out on the Ouirin wringer described in Chapter 14.

A stuffing mill is a drum equipped with an arrangement for heating its contents, usually by means of hot air. Fig. 301 shows the Turner hot-air stuffing

Entering one hollow gudgeon of the drum is a hot-air inlet and leaving the other is the air outlet. The air leaving the drum passes over series of steam coils, is heated to the desired temperature and is blown back into the drum. this way, the drum and its contents can be kept at any desired temperature. In stuffing, the water content of the leather should never be much above 50 percent and no water is added. Put pack of 600 lbs. pressed weight of leather into stuffing drum, start running and heat until temperature inside remains at 200° F. Then add a mixture of 15 lbs. of waterless moellon, 15 lbs. of oleo-stearine, 15 lbs. of Vaseline, 30 lbs. of wool grease, 10 lbs. of tallow and 8 lbs. of cod oil at 180° F. and run for 30 min., by which time all the greases should be taken up by the leather. Run cold air through the drum while running for 10 min. and then haul out the stock. Hang stock to cool to room temperature (about 2 hours) and then pack in closed boxes to condition for 48 hours. Then set out on flesh on drum machine, like that shown in Fig. 257 of Chapter 14. Hang to dry for another hour and then set out on grain on drum machine. Then hand set as smoothly as possible and send to be dried.

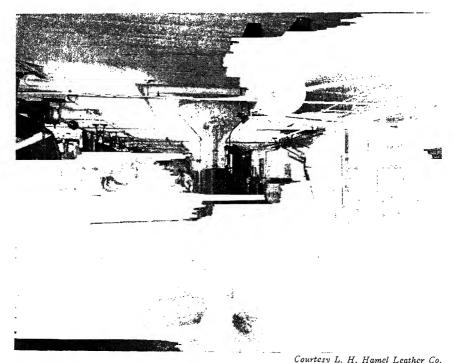


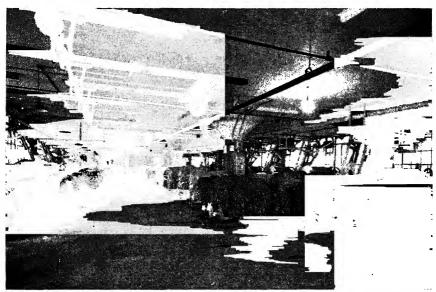
Fig. 302. Color Room Where Goatskins and Sheepskins Are Dyed and Fatliquored.

Dyeing and Fatliquoring Chrome-tanned Goatskins

The procedures given for dress-shoe upper leathers may be used, but many goatskin tanners prefer to use soap fatliquors and to dye in a single operation. One method for blacks is as follows: Put pack of 650 lbs. shaved weight into drum, start running and add 8 lbs. of borax in 100 gals. of water at 70° F. Run 20 min. and drain. Wash in running water at 70° F. for 20 min., and drain. Then add 4 lbs. of Direct Black in 50 gals. of water at 100° F., run 20 min., and drain. Add 7 lbs. of Hematine in 100 gals. of water at 100° F., run 20 min., and drain. Then add an emulsion of 5 lbs. of fig soap, 1½ lbs. of sulfonated neatsfoot oil, 7 lbs. of 20°-cold test neatsfoot oil and 6 oz. of soda ash in 50 gals. of water at 120° F. Run 30 min. and pile stock to stand over night. Next morning, set out on the machine only and then coat the grain surface of the leather with a mixture of 2 parts of glycerin and 1 part of 20°-cold test neatsfoot oil, and hang skins over poles to dry.

Stock for colors is neutralized and washed in the same way. Then add 6½ lbs. of gambier extract in 50 gals. of water at 100° F., run 10 min. and add 15 lbs. of Tamol-NNO (Röhm & Haas Co.). Run 20 min. and drain. Wash in running water at 80° F. for 30 min., and drain. Add desired amounts of acid dyes in 100 gals. of water at 120° F., run 30 min., and drain. Then add 8 lbs. of 20°-cold test neatsfoot oil and 8 lbs. of fig soap emulsified in 50 gals. of water at 120° F. Run 30 min. and pile stock over night. Next day, set out on machine, coat grain with glycerin-neatsfoot mixture and hang to dry.

Fig. 302 shows a department of a tannery where both goatskins and sheepskins are dyed and fatliquored. The steps at the right lead to reservoir tanks in which the various materials are mixed preparatory to running into the drums on either side. At the left, the stock is being piled on horses after dyeing and fatliquoring.



Courtesy L. H. Hamel Leather Co.

Fig. 303. Setting-out Room for Goatskins and Sheepskins.

Dyeing and Fatliquoring Chrome-tanned Sheepskins

There are many types of chrome-tanned sheepskin leathers, but it will be sufficient to illustrate the principles involved in dyeing and fatliquoring by giving two typical procedures. For boxing-glove leather of violet color, put 450 lbs.

shaved weight of stock into drum, wash in running water at 100° F. for 30 min., and drain. Add 18 lbs. of Tamol-NNO in 150 gals. of water at 100° F., run 30 min., and drain. Wash in running water at 100° F. for 5 min., and drain. Add 150 gals. of water at 120° F., start drum running and add 4½ lbs. of Resorcine Brown, 64 lbs. of Crocein Scarlet, 4 lb. of Wool Violet and 8 lbs. of concentrated ammonia in 36 gals. of water at 120° F. Run 15 min. and add 20 lbs. of stainless sumac extract and 4 lbs. of Hypernic crystals in 30 gals. of water at 120° F. Run 30 min. and add 9 lbs. of 90 percent formic acid in 9 gals. of water at 90° F. Run 20 min, and add 1 lb, of titanium potassium oxalate in 9 gals, of water at 70° F. Run 10 min., and drain. Wash in running water at 70° F. for 10 min., and drain. Then add 36 lbs. of Tanoyl No. 1170 (National Oil Products Co.) in 100 gals. of water at 140° F., run 20 min., and determine pH value of the liquor; if it is above 3.8, cautiously add enough dilute sulfuric acid to bring it down to 3.5. Run 5 min. longer and drain. Wash in running water at 120° F. for 5 min. and drain. Then add 6 oz. of Methyl Violet, 9 oz. of Safranine and 18 oz. of Bismarck Brown in 36 gals. of water at 120° F., run 20 min., and drain. Haul out stock, set out, and hang to dry.

For garment leather, put pack of 450 lbs. shaved weight into drum and wash in running water at 100° F. for 30 min., and drain. Add 20 lbs. of stainless sumac extract and 20 lbs. of Leukanol in 150 gals. of water at 100° F., run 30 min., and drain. Wash in running water at 100° F. for 30 min., and drain. Add 12 lbs. of Resorcine Brown and 4 lbs. of disodium phosphate in 150 gals. of water at 120° F., run 30 min., and add 20 lbs. of Tanoyl No. 1170 in 20 gals, of water at 120° F. Run 30 min., and add 12 lbs. of Tanoyl Soluble Wax No. 1778 in 10 gals. of water at 120° F. Run 10 min., and add 8 lbs. of 90 percent formic acid in 8 gals. of water at 120° F. Run 10 min. and haul out stock. Pile over night and then set out on machine and hang to dry.

Fig. 303 shows the setting-out room of a tannery making both goat and sheep leathers. The setting-out machines, of the wringer type, are located along the windows on both sides of the room.

Dyeing and Fatliquoring Heavy Glove Leathers

A procedure will be described for baseball glove and mitt leathers, which is suitable for many types of heavy glove leathers. In this procedure, the stock is given a retanning with chrome liquor and Calgon to assist in the penetration of the dyes. Regular chrome-tanned cowhides and kips are split to the desired weight and made up into packs of 1000 lbs. shaved weight each. Put pack of 1000 lbs. shaved weight into drum and wash in running water at 70° F. for 30 min., and drain. Add 70 lbs. of Calgon Flakes (Calgon, Inc.) in 80 gals. of water at 70° F. Run 1 min., and add 10 gals. of stock sulfur-dioxide chrome liquor, described in Chapter 12, which contains the reaction products of 2 lbs. of sodium dichromate per gallon. Run 2 hours, drain and wash in running water at 70° F. for 30 min., and drain. Add 100 gals. of water at 100° F. and then 1½ lbs. of aluminum sulfate in 20 gals. of water at 100° F. Run 10 min., and add 8 lbs. of borax in 20 gals. of water at 100° F. Run 15 min. and drain. Wash in running water at 140° F. for 10 min., and drain. Add 100 gals. of water at 140° F. to the drum.

Add 14 lbs. of Alisarine Yellow, 4 lbs. of Mordant Yellow and 2 lbs. of Acid Orange dissolved in 50 gals. of water at 140° F. Run 30 min., and add 60 lbs. of Leatherlubric and 60 lbs. of Sulfo-glyconeats (E. F. Houghton & Co.) in 50 gals. of water at 180° F. and run 1 hour. Then measure pH value and add enough dilute sulfuric acid to lower the pH value to 3.5. Run 30 min. longer and add 70

lbs. of Salova (Salem Oil & Grease Co.) in 35 gals. of water at 160° F. Run 30 min., and add 10 lbs. of *Fustic* in 20 gals. of water at 160° F. Run 20 min., and drain. Add 20 lbs. of colloidal clay-A (Saxe-Rushworth Co.) in 20 gals. of water at 160° F., run 20 min., and drain. Add 100 gals. of water at 120° F., run 5 min., and haul out stock. Pile over night and then set out on machine and hang to dry. This leather is ready for shipment after drying and staking.

Coloring Suede Leathers

For suède leathers, it is customary to take very small skins, such as slunks, after chrome tanning, washing and neutralizing. They may be fatliquored simply by drumming with 1 percent on shaved weight of sulfonated neatsfoot oil in 500 percent of water at 120° F. for 20 minutes, or they may be treated in the same way with 1 percent of Gardinol. After fatliquoring, they are dried, dampened back, staked and buffed on the flesh side on an over-shot buffer, as described in Chapter 16. The stock is then wet back completely and put into a drum for coloring.

For blacks, per 100 lbs. or dry leather after buffing, put pack into drum and wash in running water at 100° F. until the stock is soft and pliable (30 to 60 min.). Drain and add 10 gals. of water at 125° F. Run 5 min. and add 8 lbs. of Diazine Black H. Extra (National Amiline & Chemical Co.) in 15 gals. of water at 125° F. Run 45 min. and add 2 lbs. of hydrochloric acid (20° Baumé) in 2 gals. of water at 125° F. and run 20 min. longer, or until the dyebath has become exhausted. Then drain and add 10 gals. of water at 70° F. Run 1 min. and add $7\frac{1}{2}$ lbs. of 20°-hydrochloric acid in 2 gals. of water at 70° F. Run 10 min. and add $3\frac{1}{2}$ lbs. of sodium nitrite in 2 gals. of water at 70° F. Run 20 min. and drain. Then dry and continue as described in Chapter 16.

For colors, simply replace the Diazine Black by diazine dyes of the appropriate color. These dyes are known as *developed dyes* and are used on suède leathers to prevent *crocking*, or the rubbing off of the dye from the leather onto other materials. The manufacturers of dyestuffs are prepared to give tanners many different procedures for coloring suède leathers to get the results desired.

Fatliquoring, Dyeing and Finishing Aniline Bag and Case Leathers

This stock is either vegetable tanned or Calgon tanned, and then vegetable retanned as described in Chapter 13. After splitting and shaving, it is bleached as described for vegetable-tanned calfskins in Chapter 14. It is fatliquored only once, as described above for vegetable-tanned light leathers. It is then dried. After drying, it is dampened back to a watery content of about 50 percent and is set out as smoothly as is physically possible, the last setting out being on the grain by hand. It is then tacked out to dry. When dry, the grain is bleached by swabbing with a 1 percent solution of oxalic acid. The leather is dried again and is then dyed by spraying the grain surface with a solution of dyes to give the desired color. It is then finished by swabbing onto the grain one or more coats of properly diluted Venecian Finish (Apex Chemical Co.) as may be needed to develop a mirror-like luster when hot plated. After drying, it is plated at a temperature of 180° F. and a pressure of about 300 tons. It is then ready for delivery.

Fatliquoring Football Leathers

Leather for the official intercollegiate football is made from 50-lb. steer hides selected for practically flawless grain surface. This leather is either vegetable tanned, or Calgon pretanned and vegetable retanned, much like bag and case

leathers. It is split after tanning to give it a finished weight of 5 oz. The leather must be very plump and tight, but it must be given enough fatliquor so that the final leather has a fat content of from 18 to 22 percent. To get this high fat content by fatliquoring, it is necessary to wash the leather thoroughly before fatliquoring so that the water-soluble matter does not interfere with the fatliquoring. Follow the procedure for bag and case leathers, but fatliquor two or three times, as may be necessary to increase the fat content, drying after each fatliquoring. When making this leather for the first time, analyze the leather after drying after each fatliquoring, and repeat the fatliquoring operation until the fat content on the airdry basis equals or exceeds 18 percent.

This leather is usually made only in bends; that is, the bellies and shoulders are cut off before fatliquoring. The leather is hung to dry after setting out, and it is never tacked out to dry. When it has been dried after the last fatliquoring, it is hand-dyed on the grain to give the desired color after embossing and inflating when made up as a football. This leather needs no finishing, but it can be finished lightly to get desired effects. It is finally embossed with a pebbled embossing plate, and is ready for delivery after a light staking.

Fatliquoring White Leathers

The fatliquoring of white chrome-tanned leathers has already been described in Chapter 12.

An excellent fatliquor for white shoe-upper leathers can be made as follows: Mix 3 gals. of light paraffin oil, 2 gals. of sulfonated castor oil and 20 fl. oz. of concentrated ammonia. Stir to a smooth paste and continue to stir while adding 4 gals. of boiling water and then 2 gals. of ammonia-casein solution (1 lb. of casein per gallon). The making of casein solutions will be described in Chapter 17. Then stir in 100 lbs. of powdered titanium dioxide. Mix well and grind in a mill to a uniform paste, which is known as maxwhite paste. Mix 75 lbs. of maxwhite paste with 50 lbs. of sulfonated neatsfoot oil, 50 lbs. of 20 -cold test neatsfoot oil and 265 lbs. of water. When intimately mixed, this constitutes the white fatliquor. Fatliquor the stock with 1 lb. of this fatliquor in 10 gals. of water at 120° F. for each 100 lbs. shaved weight of stock, running 20 min., and lowering the pH value to 3.5 by the cautious addition of dilute sulfuric acid, running 10 min. longer, and then hauling out the stock to be set out and dried.

For many types of white leather, it is sufficient to use simply 1 lb. of Tanoyl No. 1170X (National Oil Products Co.) per 100 lbs. shaved weight. Some tanners of white-suède formaldehyde leathers use only 1 percent on shaved weight of Gardinol (du Pont).

Oiling and Dyeing Shearlings

In Chapter 12 the tanning of sheepskins and lambskins with the wool was described. The dyeing operation really consists in the dyeing of the wool to give the skins the appearance of more expensive furs. After the stock has been taken from the tanning vat, remove the bulk of the water from the skins by putting them through the Quirin wringer. Then stake each skin and send it to be oiled.

Fig. 304 shows a type of staking machine used on wool skins and furs. The purpose of the staking machine is to flex the leather and separate the fibers, which have been pressed together in the Quirin wringer. The machine contains three rotating arms, each with a blade at the end. The skin is laid on the flexible bed, flesh side up and the arms rub over it, flexing it just enough to

loosen up the fibers. During staking, the skin is turned after each stroke of a blade so that the entire area of the skin is finally staked.

After staking, each skin is laid out on a flat table, flesh side up and coated with oil by hand, using a sheepskin swab. The materials used for oiling usually consist of sulfonated oils, soap and alkali emulsified in water. A satisfactory mixture consists of 5 gals. of sulfonated neatsfoot oil, 1 lb. of sodium oleate soap, 1 lb. of soda ash and 20 gals. of water. This is sufficient to oil off about 500 skins. After each skin has been oiled, it is folded over double along the line of the backbone, with the oiled flesh side on the inside. The skins are piled in this folded condition and allowed to remain in the pile for about 3 hours to condition. They are then dried at 90° F. in about 9 hours and kept in the dry state for not less than one day. Then water is brushed onto the wool of each skin and the skins are piled to condition for 1 day.

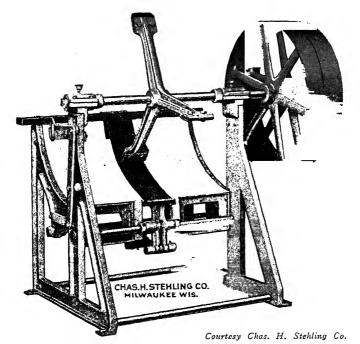


Fig. 304. Three-arm Staker for Furs and Wool Skins.

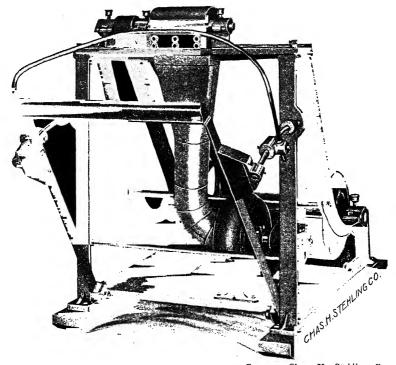
One hundred skins and 250 lbs. of dry sawdust are put into a drum and run for 1 hour. The sawdust absorbs grease and other matters from the wool and cleans it. The skins are then placed in a cage drum and run for 30 min. to free them from sawdust. The periphery of this drum is made of open wirework to permit the sawdust to escape while the skins are retained.

The wool is then clipped to a length corresponding to that of the animal whose fur the shearling is being made to resemble, usually to about § inch. Fig. 305 shows a clipping machine, which can be adjusted for the desired length of wool. A fan is attached to carry away the clippings of wool.

After clipping, the skins are still damp. Stake them again and then comb

out the wool before the skins become dry. Fig. 306 shows a combing machine. It contains a revolving *carding* roll, which passes over and through the wool, cleaning it and combing it out very smoothly. The carding roll is made like a fine-wired brush and it is 4 feet, 8 inches long. This combing operation is usually known in the trade as *carding*.

After carding, the skins are again staked and reclipped. They are then assorted for quality and finish. At this stage, while still damp, skins that are not to be dyed are toggled or tacked onto frames and allowed to dry flat. They are restaked, buffed on the flesh side to make the flesh side smooth, and then carded again.



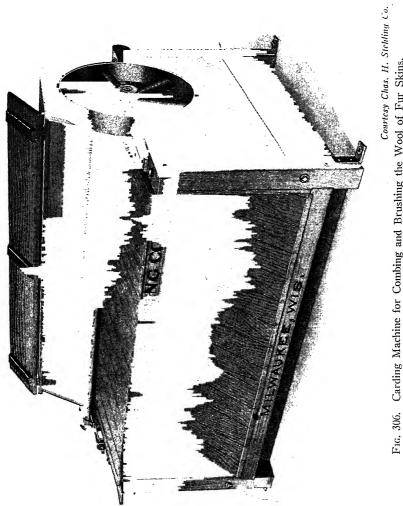
Courtesy Chas. H. Stehling Co.

Fig. 305. Wool Clipping Machine for Furs and Wool Skins.

Stock to be dyed is taken immediately after tanning, put into a drum and treated with soda ash solution. For a pack of 1000 lbs. wet weight, add 5 lbs. of soda ash in 100 gals. of water at 100° F. Run 2 hours and then drain off the liquor and wash the stock in running water at 100° F. for 30 min. Without this treatment with soda ash, the wool would not take up the dyes readily. An ancient name for this operation is *killing*. Killing the wool really means simply preparing it to take the dye; in this case, soda ash is a killing agent.

The skins are then put through the Quirin wringer and put back into the drum for mordanting the wool. This is often done with a solution of copperas, common salt and acetic acid, the stock being left in the liquor at 100° F. over

night. There are many different types of mordants, each combining first with the wool and subsequently with the dyestuff. For the mordants and dyestuffs used to get any desired color on the wool, the reader is referred to the many manufacturers of dyestuffs for wool. After mordanting, the stock is again passed through the Quirin wringer and dyed, usually with oxidation dyes that require



Carding Machine for Combing and Brushing the Wool of Fur Skins

oxidation after dyeing to develop the true colors desired. With some oxidation colors, the stock is first treated in the drum with solutions of the dyes, and then with hydrogen peroxide and ammonia to develop the color. After coloring, the stock is washed in running water. It is then again put through the Quirin wringer, and from this point on is treated just like the stock put through the Quirin wringer immediately after tanning and not to be dyed, as described above. In other words, it is staked, oiled, dried, dampened, drummed with sawdust,

clipped, carded, reclipped, and toggled to dry. The stock is then restaked, buffed on flesh side, carded and the wool is treated with special finishing oils and iron. The stock is then staked once more and recarded, after which it is ready for shipment.

Fats and Oils Used in Fatliquoring and Stuffing

In most of the procedures given above, specific oils were mentioned, but it must not be assumed that they are necessarily the best oils to use, or that there may not be many other oils that would prove as satisfactory as those described. It is possible that any oil or fat might find some useful place in the leather industry. It is helpful to many readers to know just what materials may be used in order to get a satisfactory result, and we have given the names of specific materials known to have given satisfactory results on a large scale. There may be many others.

Tanners are desirous of securing the cheapest materials available that will give them completely satisfactory results. Prices of oils change with market conditions, and the cheapest oil today for a given purpose may not be the cheapest at some other time. An oil that will best serve for making one grade or kind of leather may not be best for another. It is advantageous for a tanner to become familiar with the prices and properties of all oils on the market. This is a big subject and many volumes have been devoted to it; we could not hope to do justice to it in the small amount of space allowed to it in this book. Instead of attempting to list all available oils, with their average analyses and properties, it seems better to devote the space allowed to certain general properties of oils that mean most to a tanner.

Spews

Many tanners have been seriously troubled by spews forming on the grain surface of their finished leathers. The common white spew usually consists of crystals of solid fatty acids, such as palmitic or stearic acid. Practically all fatty oils consist of compounds of glycerin and fatty acid. In many cases, the glyceride of the oil is liquid at room temperature while the fatty acid is solid. Although a glyceride (a compound of glycerin and fatty acid) may penetrate into the leather as a liquid, conditions within the leather are such that the glyceride readily tends to break down into glycerin and free fatty acid. If the fatty acid is solid at room temperature, it tends to crystallize out on the grain surface of the leather as a spew. The formation of spew is favored by high acidity of the leather, high fat content, dampness and low temperatures.

When a tanner is troubled by such spews, he should have all the oils and fats that enter his leather examined to get the melting point of the liberated fatty acids. If the melting point of these fatty acids is much above 70° F., he would do well to change to oils whose free fatty acids have a lower melting point. When oils are cold-pressed, the fractions of higher melting point are removed. Many tanners use neatsfoot oil in fatliquoring and specify the 20°-cold test product simply to make sure that no fatty acids of high melting point likely to cause spew are introduced into the leather. To guard against spews, a tanner should be extremely careful in selecting oils whose liberated fatty acids are liquid at room temperature.

Gummy Spews

Manufacturers of heavily stuffed leathers, particularly those using large quantities of raw cod oil sometimes are troubled with gummy spews on their leathers

These spews look like the globules of rosin that sometimes spew out onto the surface of pine boards. The liberated fatty acids of cod oil are very reactive chemically. They not only combine with hide protein to produce a chamoising effect, but they combine readily with oxygen from the air. In the course of their oxidation, they become first the sticky, resinous material that composes the gummy spew; with further oxidation, they become solid. Air is essential to the formation of this type of spew. In a pile of leather, a tanner will find this spew only along the edges of the leather exposed to the air.

Such spews are extremely annoying. When they occur, a change in method of stuffing is desirable. The leather already spewed can be saved by removing the spew with solutions of soda ash. The spew consists of resinous acids that react readily with soda ash, producing water-soluble resin soaps. The method of removal consists in wetting the leather back in a drum with water at 120° F., adding about 5 lbs. of soda ash per 100 lbs. of dry leather and drumming for an hour. The leather is then washed in running water at 120° F. for about 30 min.

In order to avoid a recurrence of the spew, it is desirable to decrease the proportion of raw cod oil in the stuffing mixture and replace it by materials which do not have readily oxidizable fatty acids. Often the replacement can satisfactorily be made by using chamois moellon degras, from which a large portion of the oxidizable fatty acids was removed in chamoising.

Soaps consist of chemical combinations of fatty acids with alkali metals, such as sodium and potassium. Since most leathers are of acid reaction, the free fatty acids of soaps are liberated almost instantaneously upon entering the leather. It is, therefore, of very great importance to the tanner to know that soaps with solid fatty acids may contribute to the formation of white spews and those with oxidizable fatty acids may contribute to gummy spews. As a double safeguard, many tanners use only soaps consisting essentially of pure sodium oleate. Free oleic acid is a liquid at temperatures above 57° F. and could not form spews at temperatures above this.

What Fatliquoring Does to Leather

Even though the making of leather consists of a long series of exceedingly complex chemical reactions, the writer had tried to avoid scientific discussions so as not to confuse readers not versed in science. Because it is of such tremendous practical importance to the tanner in fatliquoring, drying and staking leather to go a little more deeply into theory, the writer is going to try to explain what happens during fatliquoring, and its effect on the subsequent operations. It will take but very little space in this chapter, and the reader with a distaste for theory can simply skip on to the next section of the chapter without any loss of time in reading.

In order to make our story clear, we must go back to the production of hide fibers and their constituent fibrils, as described in Chapter 1. White corpuscles from the blood, called *fibroblasts*, migrate up through the skin, from the flesh side to the grain surface. As they go, they exude a protein solution, which subsequently sets to jelly and hardens into a fibril. Keeping this in mind, let us now take an ounce of gelatin and dissolve it in a quart of hot water, mix well and allow it to cool. If the cooling it done rapidly, when room temperature is reached, the solution will still be quite fluid. However, if we examine it carefully over the minutes that follow, we will note that the solution is increasing in viscosity, and that after a time the viscosity is vastly increased; that is, the solution becomes

a solid jelly. When the jelly is dried by allowing the water to evaporate, a solid mass of gelatin of enormous tensile strength is obtained.

According to our theory, the very fluid gelatin solution, when first prepared, contained many tiny particles, or molecules, of gelatin not touching one another. Gelatin molecules contain both acid and basic groups and the acid group of one molecule can combine with the basic group of another, if they come into contact. During the standing of the cooled gelatin solution, the molecules slowly turn, like the needle of a compass, so that the acid group of one turns towards the basic group of a neighboring molecule, and finally the two combine. In the course of this series of combinations, molecules of increasing size are formed. As the average size of the molecule increases, the viscosity of the solution increases, until finally all the original molecules are linked together in the form of a three-dimensional network occupying the entire volume of the original solution, converting it to a solid jelly, with the water in the interstices of the network structure of solid gelatin.

Keeping this in mind, let us now take a sheet of dry gelatin and cut out two strips, say 1 by 6 inches each, and lay one strip over the other. They show no tendency to cohere. Now let us soak these two strips in cold water over night. They will then be found to have increased greatly in volume by absorbing water. If we now place one strip over the other, they still show no tendency to cohere. But now, let us place one strip over the other and allow them to dry out while in contact. When dried, they will be found to stick together with a force approaching, but not quite equalling, the forces that make up the tensile strength of a single strip of the dry gelatin.

What has happened is that combinations have taken place between surface acid and basic groups of the two strips. Since the acid and basic groups in the strips of jelly cannot move as freely as in a solution, the combinations at the surface of contact of the two strips are not as complete as in the solution setting to a jelly; consequently the forces of cohesion between the two strips can never quite equal those of the tensile strength of a single strip of gelatin, but they are, nevertheless, very great. If we ponder over the growth of the skin on a living animal, we get some idea as to what holds the entire structure together and gives it its strength.

Now let us take a bated skin and dry it without any other treatment. It shrinks and becomes a hard, compact mass with all the fibers cohering with enormous forces, giving the skin a tremendous tensile strength. Now let us take another bated skin and soak it for three days in successive changes of acetone to remove all the water, and then let the acetone evaporate. The skin does not dry hard, but soft and flexible, and it resembles a beautiful skin of white leather. By removing the water before drying out the acetone, the combination of the acid and basic groups at surfaces of contact of fibers was prevented.

Now let us go back to our strips of wet gelatin and coat them with oil over the surfaces of contact. It will be found that their tendency to cohere decreases very rapidly with increasing amount of oil applied. If enough oil is used, no cohesion takes place.

When scientific men attempt to explain complex phenomena to laymen, they usually resort to analogies between the complex phenomenon and something with which the layman is familiar. For example, chemists have explained the fundamental action of fatliquoring to the layman as a *lubrication* of the fibers so that they may slide over each other and give the leather flexibility and strength. The example of the bated skin soaked in acetone before drying shows that the fundamental action is not one of *lubrication*, but of *preventing cohesion* of the fibers

during drying. With all this in mind, many effects of changes in fatliquoring, drying and staking become clearer.

Effect of Depth of Penetration of Oils into Leather

In experimenting with various fatliquors, Wilson, Merrill and Daub found that fatliquors which penetrate deeply into leathers have a tendency to make them loose. Using increasing amounts of oils of increasing penetrating powers, in several series of tests, they found that the leathers improved in quality up to a maximum and that then a loosening of the flanks became observable while the butts were still improving in quality. Using still greater amounts of oil, the leathers became loose all over. If the function of the fatliquor was *only* to lubricate the fibers, this should not have happened.

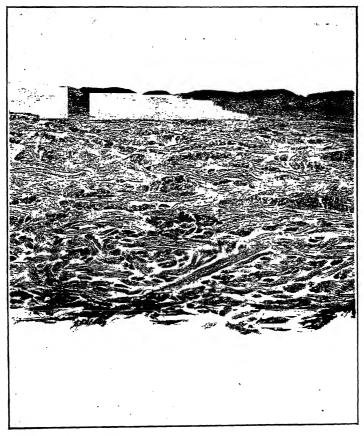


Fig. 307. Cross-section of Flank of Chrome Calf Fatliquored with Fatliquor of Lower Penetrating Properties.

Location: flank.

Thickness of section: 40 microns, or 0.00158 inch.

Magnification: 50 diameters.

In one test they fatliquored two packs of chrome-tanned calfskins with the same total amounts of oil, but one with a fatliquor of great penetrating properties and the other with a less stable fatliquor. After the packs of leather had been dried, although they both contained the same amount of oil, the leather was very different physically. Where the fatliquor of high penetrating properties was used, the leather was clearer and brighter in color than the other pack and the butt areas were generally finer, but the flanks were so loose and puffy that the cutting value of the leather for shoe uppers was greatly reduced.



Fig. 308. Cross-section of Flank of Chrome Calf Fatliquored with Fatliquor of Higher Penetrating Properties.

Location: flank.

Thickness of section: 40 microns, or 0.00158 inch.

Magnification: 50 diameters.

Figs. 307 and 308 show cross-sections of the flanks of skins taken from the two packs, respectively.

They also took a flank from each pack and split it on the splitting machine

content. From the results obtained, they constructed the chart in Fig. 309, showing the oil content of the leather at different depths from the grain to the flesh. In the tight flank the bulk of the oil was present in the grain and flesh layers, with practically none in the middle layer. In the loose flank, the oil was much more uniformly distributed, having much less in the grain and flesh layers and a considerable amount in the middle layer.

What happened to make the flanks of the one pack loose is evident from the theoretical discussion above. Where no oil penetrated into the middle layer, the fibers of the leather cohered on drying, and these cohesions kept the leather tight and compact. Where the oil penetrated completely through the thickness of the leather, the number of cohesions between fibers was greatly lessened, and so the fibers of the leather after drying were separated, giving the leather a loose and spongy structure.

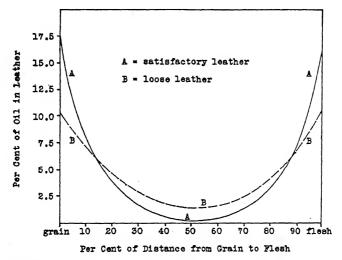


Fig. 309. Distribution of Oil Through the Thicknesses of Tight and Loose Flanks of Chrome-tanned Calf Leathers.

If there were no cohesions at all, the leather would separate into its constituent fibrils and we should have no leather structure at all. On the other hand, if all the fibrils and fibers cohered, we would have a skin in the form of a hard and horny structure, with no real value as leather. Somewhere between these two extremes, we have the ideal leather for any given purpose. It would take the calculations of an Einstein to determine the distribution of cohesions required for any ideal leather. Practically, the problem is not so difficult because we already have detailed procedures for making many perfectly satisfactory kinds of leather. But through a more intimate knowledge of these cohesions and methods of making and breaking them, we can hope to arrive at improved methods for making leather increasingly suitable for special needs.

Sulfonated Oils

Although most oils are insoluble in water, the fatty-acid portions of the oils can be given limited water solubilities by converting them into soaps, on the one hand, or into sulfonated oils on the other. In the case of a simple soap,

the water-insoluble fatty acid is combined with very soluble sodium or potassium, and the alkali metal carries the fatty acid into solution. When strong acid is added to a soap solution, it forms a salt with the alkali metal and the liberated fatty acid is immediately thrown out of solution.

Most sulfonated oils are really soaps, but the fatty acid has a soluble sulfonic group combined with it, which tends to give it a limited water solubility, even when the soap is decomposed by adding acid. This sulfonic group also enables the sulfonated fatty acid to enter into a loose combination with the chromium of chrome-tanged leathers.

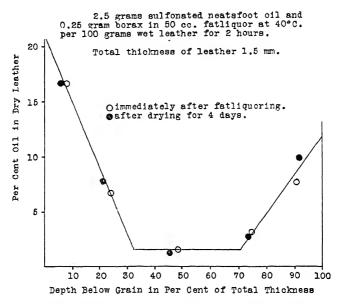


Fig. 310. Distribution of Oil through the Thickness of Chrome-tanned Calf Leather After Fatliquoring with Sulfonated Neatsfoot Oil.

Working under the writer's direction, Merrill carried out a great many experiments on the fatliquoring of chrome-tanned calf leathers with sulfonated neatsfoot oil that are worthy of the tanner's careful study. A chrome-tanned calfskin was cut into strips weighing 100 grams each in the wet state, and each strip was fatliquored for 2 hours at 104° F. with 50 cc. of fatliquor, except as otherwise noted. The strips were split into 5 layers after fatliquoring, either before or after drying, and each layer was analyzed separately to determine the amount of oil at different depths below the grain surface.

In the first two tests, a strip of 100 grams was fatliquored with 50 cc. of fatliquor containing 2.5 grams of sulfonated neatsfoot oil and 0.25 gram of borax. In the first test, the leather was split into 5 layers after fatliquoring and drying; in the second test, it was split before drying. The results of both tests are shown in Fig. 310. In depths from 30 to 70 percent, the oil found is apparently that originally present as natural animal fat. The sulfonated oil apparently penetrated

to a depth of 30 percent both from the grain and flesh sides, although the grain side received more oil than the flesh side. Since the strip split before drying has the same distribution of oil as it had after drying, it is apparent that the oil did not penetrate further during drying. When raw oils are used, this effect is very different; during drying, the oils continue to spread over the wet surfaces of the fibers, and oils leave the surfaces and penetrate into the interior of the leather. This is one of a number of reasons for believing that sulfonated oils combine with chrome-tanned leathers.

In the second series of tests, the 50-cc. portions of fatliquor contained increasing amounts of both sulfonated neatsfoot oil and borax; for each 10 grams of oil, 1 gram of borax was added. Fig. 311 shows the total amount of oil taken up by the leather

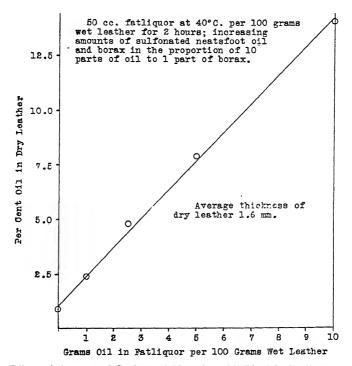


Fig. 311. Effect of Amount of Sulfonated Neatsfoot Oil Used in Fatliquoring Chrometanned Calf Leather on the Amount Taken Up by the Leather.

without regard to its penetration. It increases in direct proportion to the amount of oil added. Approximately two-thirds of the total amount of oil added was taken up by the leather, and one-third remained in the liquor.

Fig. 312 shows how the oil taken up by the leather was distributed throughout its thickness. With a small increase in amount of oil used, there is no increase in penetration, but when the amount of oil is increased tenfold, the oil penetrates deeply into the leather. This is further evidence that the sulfonated oil combines with the chrome-tanned leather and does not spread until an excess over the amount capable of combining with the leather is present.

In the third series of tests, the amount of oil used was kept constant at 2.5 grams per 100 grams of wet leather, but the amount of water was increased. As the fatliquor was diluted with increasing amounts of water, the quantity of oil taken up by the leather decreased. When the volume of fatliquor containing 2.5 grams of oil was 50 cc., the dry leather contained 4.8 percent of oil, but when the fatliquor was diluted to 200 cc. with water, the dry leather contained only 3.0 percent of oil. On the other hand, the depth of penetration of the oil remained practically the same.

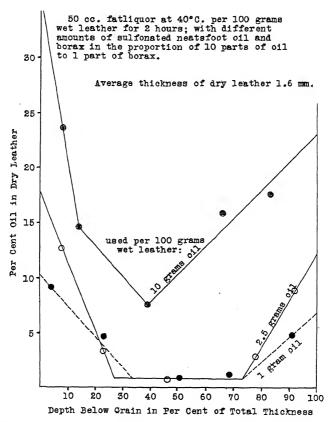


Fig. 312. Effect of Amount of Sulfonated Neatsfoot Oil Used in Fatliquoring Chrometanned Calf Leather Upon the Penetration of the Oil into the Leather.

The fourth series was run to determine the effect of time of fatliquoring. The results, shown in Fig. 313, are plotted in two different ways. The upper curve shows the percentage of total oil added which was taken up by the leather; in other words, after 4 hours the 100 grams of wet leather had taken up 85 percent of the 2.5 grams of oil added. The lower curve shows the percentage of oil found in the dry leather multiplied by 10, so that the same scale could be used to advantage. The effect of time on the penetration is shown in Fig. 314 for fatliquoring times of 30 minutes and 7 hours. For the fixed amount of 2.5 grams of sulfonated neatsfoot

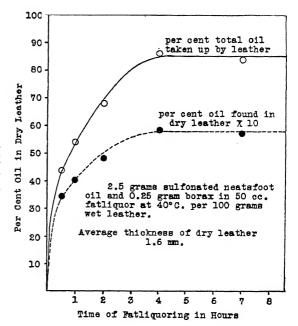


Fig. 313.

Progress in the Absorption of Sulfonated Neatsfoot Oil by Chrometanned Calf Leather with Time of Fatliquoring.

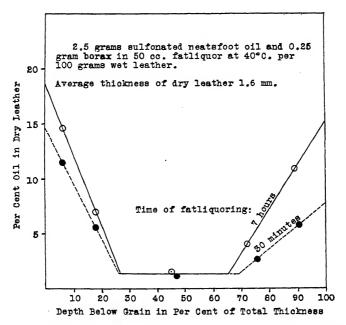


Fig. 314. Penetration of Sulfonated Neatsfoot Oil Into Chrome-tanned Calf Leather as a Function of Time of Fatliquoring.

oil per 100 grams of wet leather, the time of fatliquoring has practically no effect on the depth of penetration of the oil into the leather. All the increased amount of oil taken up by the leather remains in the outer layers.

A fifth series was run to determine the effect of pH value of the fatliquor. In this series, only the pH values of the fatliquors were increased by adding increasing amounts of soda ash. The pH values of the fatliquors increased from 5.1 to 8.1 after fatliquoring. Fig. 315 shows the results for final pH values of 5.15 and 8.07, and also for a series in which 0.39 gram of olive-oil soap and 0.94 gram of soda ash were added, the final pH value being 8.47. In the chart, Na₂CO₃ means soda ash.

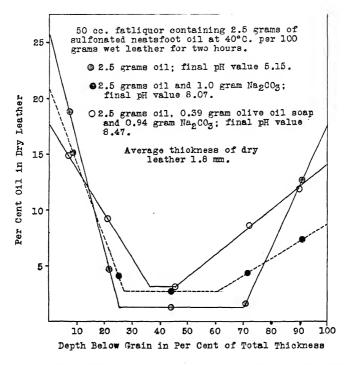


Fig. 315. Effect of pH Value and of Soap on the Penetration of Sulfonated Neatsfoot Oil into Chrome-tanned Calf Leather.

Increasing the pH value had no effect on the total amount of oil taken up by the leather, but it had a definite effect in increasing the depth of penetration of the oil.

A sixth series was run in which the strips of leather were kept for 2 weeks in sodium phosphate solutions with pH values adjusted over a range from 3.0 to 9.0. They were then fatliquored with equal portions of the same fatliquor. In this series, 100-gram portions of wet leather were fatliquored with 100-cc. portions of fatliquor containing 4 grams of sulfonated oil and 0.4 gram of borax for 2 hours at 104° F. The results are shown in Fig. 316 for the leathers pretreated with phosphate solutions of pH values 4.0 and 9.0. There was essentially no difference in total oil taken up by the leather, but the depth of penetration was greater for the higher pH

value. In this case, the results were complicated by the combination of phosphate with the chrome of the leather, which assists in the penetration of the sulfonated oil.

Sulfonated neatsfoot oil appears to penetrate chrome-tanned calf leather to a depth of about 30 percent from both grain and flesh sides and then stop, unless great excesses of oil are used. The reason for this appears to be the fact that the neutralization of the leather in practice is only superficial, and sulfonated oil penetrates only to the depth that the leather has been neutralized. With increasing pH value, the vigor of combination of the oil with the leather is decreased and the oil penetrates more deeply. A knowledge of this fact has led to the now well established practice of starting the fatliquoring operation at higher pH values to get the necessary penetration and then acidifying to a pH value between 3.5 and 4.0 to get greater fixation of the oil by the leather.

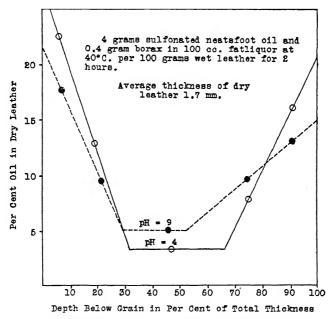


Fig. 316. Effect of Pretreatment of Chrome-tanned Calf Leather with Sodium Phosphate Solutions of Different pH Values on the Penetration of Sulfonated Neatsfoot Oil into It.

Egg Yolk

The commercial egg yolk used by the leather industry is usually made from eggs condemned as unfit for human consumption. About 100 lbs. of deshelled eggs and 20 lbs. of common salt are thoroughly mixed and sold as tanners' egg yolk. A salt-free egg yolk is also available in which the salt is replaced by a small amount of preservative. An average analysis of the salted egg yolk is water 59.4 percent, protein 11.0 percent, fats 10.4 percent, other organic matter 0.4 percent and ash 18.8 percent, while that of the salt-free egg yolk is water 71.5 percent, protein 13.0 percent, fats 13.2 percent, other organic matter 0.5 percent and ash 1.8 percent.

The use of egg yolk in fatliquoring colored, chrome-tanned calf leathers has already been described above. Its use results in fine grain, desirable feel and very uniform and clear colors.

Wilson, Merrill and Daub made a study of the emulsifying power of whole egg, the white, and the yolk as used in an ordinary fatliquor and of the effect of the fineness of the emulsion upon the quality of chrome calf leather. Equal parts of sulfonated neatsfoot oil and neutral neatsfoot oil were mixed. In each test, 10-gram portions of this mixture were mixed with varying amounts of whole egg, white or yolk and water at 100° F. to make a final volume of 100 cc. The pH values of all the emulsions lay between 7.0 and 7.1. The mixtures were shaken vigorously

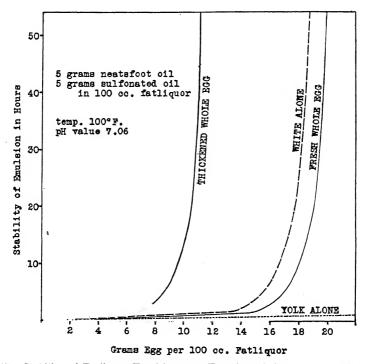


Fig. 317. Stability of Fatliquor Emulsion as a Function of Amount of Added Whole Egg, Egg White or Egg Yolk.

and poured into tall cylinders. The stability was measured by the lapse of time before there was a perceptible separation of oil and water. The results are shown in Fig. 317.

The white alone had the greatest stabilizing action and the yolk alone the least. When the mixed whole egg is allowed to stand for several weeks, it begins to thicken, but with no apparent change in water content. When the thickened egg is used, it increases the stability much more than when the fresh egg is used.

Fig. 318 shows a photomicrograph of an egg-yolk fatliquor containing ½ 1b. of sulfonated neatsfoot oil, 1½ lbs. of commercial egg yolk and 1 lb. of borax per gal. of water. It appears to contain extremely tiny globules of oil interspersed between masses of flocculent albumen.

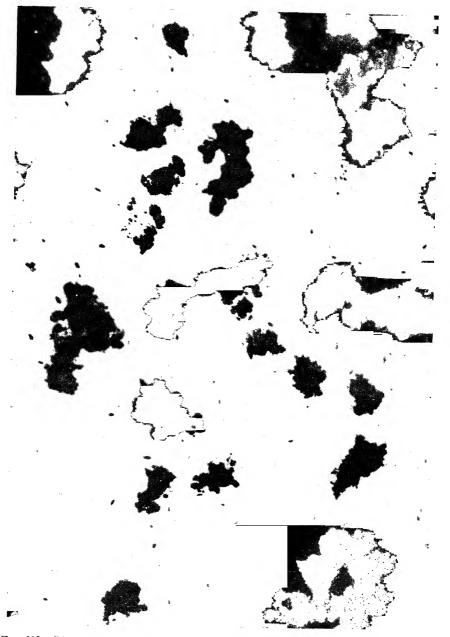


Fig. 318. Photomicrograph of Fatliquor Containing & Lb. of Sulfonated Neatsfoot Oil, 1& Lbs. of Commercial Egg Yolk and 1 Lb. of Borax per Gallon of Water.

Magnification: 412 diameters.

Merrill studied the effect of adding egg yolk to sulfonated neatsfoot oil on the depth of penetration of the oil into chrome-tanned calf leather during fatliquoring. In one test, 100 grams of wet chrome calf leather was fatliquored with 50 cc. of fatliquor containing 2.33 grams of sulfonated neatsfoot oil and 0.25 gram of borax for two hours. In the other test the 50 cc. of fatliquor contained 1.5 grams of sulfonated neatsfoot oil, 6 grams of salted egg yolk and 0.25 gram of

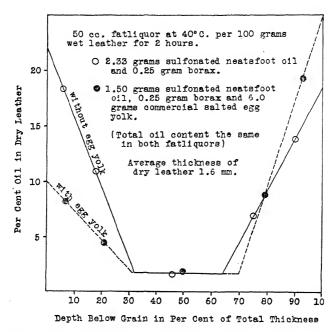


Fig. 319. Effect of Egg Yolk on the Distribution of Oil throughout the Thickness of Chrome-tanned Calf Leather during Fatliquoring.

borax. The effect of the egg yolk upon the distribution of the fat throughout the thickness of the leather is shown in Fig. 319. The egg yolk actually causes the oil to be taken up preferentially by the flesh side of the skin, which, obviously, has many advantages. Many other tests were run and this effect was found in every one. It was also found to result from the addition of salt-free egg yolk, whole fresh egg, fresh white or fresh yolk. It was not found when dried egg albumin was dissolved in water and added.

The effect of egg yolk in causing the oil to be taken up preferentially by the flesh side of the leather is shown more strikingly in a series of experiments with

Table 43. Effect of Commercial Egg Yolk upon Distribution of Oil Throughout
Thickness of Leather in Fatliquoring

Grams Egg Yolk Used	Per Cent	Per Cent Total Oil Found in			
per 100 Grams Wet Chrome Calf Leather	Oil Found in Dry Leather	Grain Layer G	Flesh Layer F		$_{ m G/F}$
None	4.26	30	18		1.67
2	4.85	19	16		1.19
4	5.78	21	29		0.72
8	6.52	14	32		0.44

variable amounts of egg yolk. 100-gram portions of wet chrome calf leather were fatliquored with 50 cc. of fatliquor containing 1.5 grams of sulfonated neatsfoot oil, 0.25 gram of borax and increasing amounts of salted egg yolk. The leathers were split into layers and analyzed. Table 43 gives the amount of egg yolk used, the percent of fat found in the dry leather, the percent of the total oil in the leather which is present in the grain and flesh layers, each having a thickness of one-tenth of that of the whole leather.

With increasing amount of egg yolk used in fatliquoring, the total fat content of the leather increases, as would be expected, but the amount of fat in the grain layer decreases. If no egg yolk is present, the grain layer receives 1.67 times as much oil as the flesh layer. When 8 grams of egg yolk per 100 grams of wet leather is used, the grain layer receives only 0.44 times as much oil as the flesh layer. This power of egg yolk to cause the oil to be taken up preferentially through the flesh side of the leather is of very great practical value in giving the leather a clearer color and tighter grain.

This effect of egg yolk can also be produced by using the egg whites alone, but the use of the whole egg gives a practical result decidedly superior to that obtained with the white alone. The egg white causes the same preferential absorption of oil through the flesh side of the leather as is obtained with the whole egg, so it may be concluded that the constituents of the yolk exert some beneficial effect on the leather in addition to that resulting from preferential absorption of oil through the flesh layer.

The writer suspected that the lecithins of egg yolk might be responsible for many of the desirable properties incorporated into leather by the use of egg yolk in fatliquoring. Experiments with the lecithins obtained from soybean seem to bear out this suspicion. Commercial fatliquors containing lecithin are now available. The lecithin molecule contains a phosphorus atom associated with three oxygen atoms, forming a grouping that is present in the Calgon molecule. This led the writer to suspect that metaphosphate groups might be incorporated into the molecules of many types of oils to very great advantage; therefore he proceeded to make phosphorated oils by treating various oils with phosphorus pentoxide.

Phosphorated Oils

It is well known that various sodium phosphates combine so vigorously with the chromium of chrome leather that they will displace combined sulfate quantitatively. This suggested the idea that phosphorated oils would combine with chrome-tanned leathers much more vigorously than sulfonated oils would. The writer succeeded in phosphorating most of the oils used in fatliquoring leather, and such phosphorated oils are now commercially available.

It was also suspected that the metaphosphate group in a phosphorated oil would combine directly with hide protein just as Calgon does, the vigor of combination increasing with decreasing pH value.

Phosphorated oils combine very vigorously with all kinds of leather, but they do not penetrate very well when used alone. For this reason, they are almost always used together with sulfonated oils. Fig. 320 is a photomicrograph of a fatliquor containing $\frac{1}{2}$ lb. of phosphorated soybean oil and $\frac{1}{2}$ lb. of sulfonated soybean oil per gallon.

The uses of Tanoyl No. 1170 (National Oil Products Co.) for both vegetable-tanned and chrome-tanned leathers have been described in the procedures given above. This is a blend of phosphorated cod oil, sulfonated cod oil and chamois moellon degras which can be used to advantage on any kind of leather, except

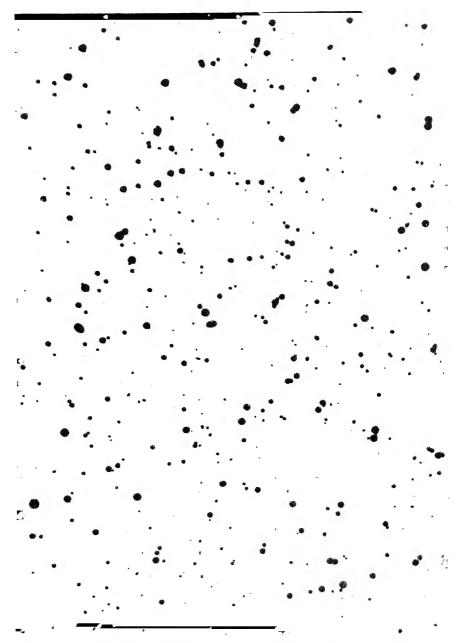


Fig. 320. Photomicrograph of Fatliquor Containing & Lb. of Phosphorated Soybean Oil and & Lb. of Sulfonated Soybean Oil per Gallon.

Magnification: 412 diameters.

white leathers and leathers of pastel shades, where the slight color imparted by cod oil might be undesirable. Tanoyl No. 1170X is a mixture of phosphorated and sulfonated coconut oils suitable for whites and pastel colors.

Moellon Degras

The oil left after chamoising sheepskins is sold commercially under the name of *moellon degras*. This is a very valuable fatliquoring material, being particularly suitable for fatliquoring vegetable-tanned leathers. Fig. 321 is a photomicrograph of a typical moellon-degras fatliquor containing 0.28 lb. of moellon-degras, 0.19 lb. of raw cod oil, 0.17 lb. of fig soap and 0.24 lb. of soda ash per gallon. Some of the larger oil globules appear to be emulsions of water in oil. Fatliquors practically always consist of emulsions of oil in water, but in moellon-degras fatliquors, we frequently find globules of oil consisting of emulsions of water in oil. Moellon degras apparently still retains some of the chamoising properties of cod oil and helps to give the leather a full and mellow feel.

Mineral Oils

Paraffin and other mineral oils are seldom used in large quantities on light chrome-tanned leathers because they do not appear to combine with the leather; they penetrate deeply into it during the drying operation by spreading over the wet surfaces of the fibers, and this has a tendency to make the leather loose. For heavier leathers which are apt to be too tight, the use of mineral oils is often very advantageous in imparting a desired mellowness to the leather.

A fatliquor of mineral oil can be prepared as follows: Mix 10.4 lbs. of oleic acid with 5 lbs. of refined white paraffin oil and then add 4 lbs. of triethanol-amine (Carbide & Carbon Chemicals Corp.). Mix thoroughly until a clear viscous solution is obtained. Then add 80 lbs. more of the paraffin oil and mix well. This may now be diluted with water to any desired extent. It may be used alone or in mixtures with other fatliquors.

Stuffing Greases

In stuffing leathers, the oils and greases penetrate completely through the leather because they depend for their penetration upon their powers to spread over wet surfaces. They are usually applied to leathers that would otherwise be very tight and firm. In selecting the proper oils and greases, the tanner is much concerned with their melting points, viscosities at different temperatures and amounts that may be used without causing excessive looseness or greasiness.

Colloidal Clays

Manufacturers of white leathers frequently use colloidal clays together with the fatliquor to get the proper softness and feel to the leather. Some tanners of shoe-upper leathers also use colloidal clays to get additional fullness and softness to the leather. The clay is usually added immediately before the fatliquor. When the stock is in the drum ready to receive the fatliquor, mix 3 lbs. of colloidal clay-A (Saxe-Rushworth Co.) with 3 gals. of water at 120° F. per 100 lbs. shaved weight of stock in the drum, add to the drum, run 5 min. and then add the fatliquor. The clay is so finely divided that it readily penetrates into the outer layers of the leather and is carried in still further by the fatliquor. The use of clay in making glove leathers is very desirable in giving the leather a fine, smooth and silky feel.

When English kaolin is subjected to a process of flotation, it separates into two portions: 10 percent remains in suspension in the water and 90 percent sep-

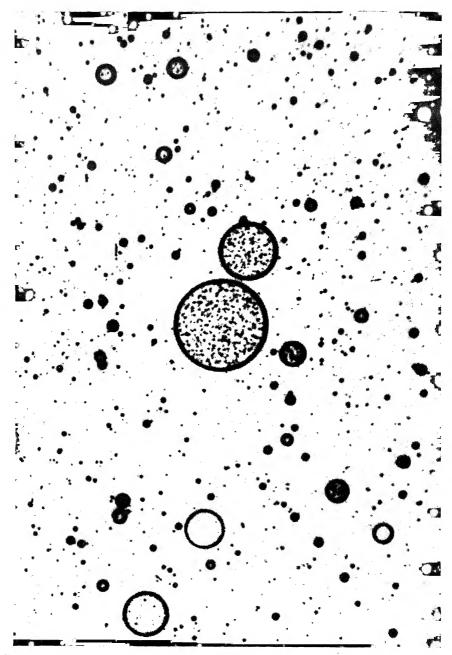


Fig. 321. Photomicrograph of Fatliquor Containing 0.28 Lb. of Moellon Degras, 0.19 Lb. of Raw Cod Oil, 0.17 Lb. of Fig Soap and 0.24 Lb. of Soda Ash per Gallon.

Magnification · 412 diameters

Fig. 322. S. & R. Brand "A." English Colloidal Clay.

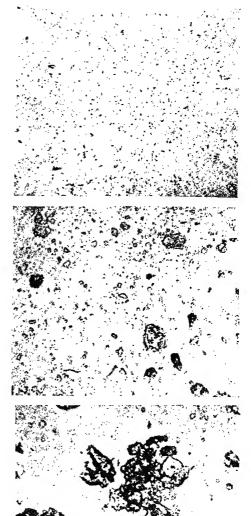


Fig. 323, S. & R. Brand "B." English Colloidal Clay.

Fig. 324.
Ordinary Washed Clay.

Courtesy Saxe-Rushworth Co.

arates out as an insoluble powder. The 10 percent remaining in suspension is known as English Colloidal Clay. In practice, the colloidal clay is separated further into two fractions, the more finely divided of which is known as Brand "A" and the less finely divided as Brand "B." Fig. 322 shows a sample of Brand "A" highly magnified and Fig. 323 shows a sample of Brand "B" at the same magnification. Fig. 324 shows a sample of ordinary washed clay at the same magnification.

The colloidal clays are entirely unlike the ordinary clays used in leather manufacture in the extreme fineness of the particles, which permits them to penetrate deeply into the leather. The writer made a number of tests on various clays in which 1 lb. of clay was mixed with 1 gal. of water and allowed to stand for an hour. 78 percent of the colloidal clay-A still remained in suspension; 9 percent of colloidal clay-B remained in suspension and only 4 percent of the ordinary soluble clay remained in suspension. Under a microscope, the writer measured the average size of the particles of colloidal clay-A and found them to be less than 0.00004 inch in diameter. Colloidal clays are composed chiefly of aluminum silicates.

Aniline Dyestuffs

In the procedures given above, the uses of some specific dyestuffs were mentioned, but this does not do justice to the enormous variety of dyes used by tanners. In the hope of getting together for the reader some useful information on most of the dyes used on leather, the writer invited the coöperation of a number of dyestuff manufacturers. To be included in this book, it was necessary that such information be very greatly condensed, because a reasonably full treatment would require an entire book the size of this one.

Messrs. R. Tiedemann and O. W. Bertram of the Commonwealth Color & Chemical Co. prepared for this book the information contained in Table 44. It is necessary to explain both the headings and the letters that designate the properties of the dyes. The first column gives a list of the dyes with Commonwealth's trade name. If the dye is also made by other manufacturers, the Color Index Number is given in the second column, which identifies it. In the next 8 columns are given data on the behavior of the dye on different types of stock, "Chrome" meaning chrome-tanned stock, "Bark" meaning vegetable-tanned stock, "Form" meaning formaldehyde-tanned stock, and "Syn. Tans" meaning stock tanned with syntans. Under each kind of tannage, "Gr." means full-grain stock and "Su." means suède leather. "Exh." means exhaustion. "Pen." refers to the depth of penetration of the dye. "Grain & Flesh Rel." refers to the relative takeup of dye by the grain side or flesh side of the leather. The next column refers to the behavior of the dyed leather upon glazing, and the last column classifies the dye as to whether it is an acid dye, a basic dye, a direct dye or a chrome dye.

The behavior or effect of the dye is indicated by letters under the headings which have the meanings given in the following key:

Key to Table 44.

E Excellent G Good F Fair	P Poor U Uneven
FH Flesh Heavier FSH Flesh Slightly Heav FL Flesh Lighter FD Flesh Duller FR Flesh Redder FY Flesh Yellower FGr Flesh Greener FBk Flesh Blacker	GH Glazes Heavier GSH Glazes Slightly Heavier GMH Glazes Much Heavier GSL Glazes Slightly Lighter T True GSY Glazes Slightly Yellower GSB Glazes Slightly Bluer GSGr Glazes Slightly Greener
B Bronzes GBL Good But L Gr. Grain Su. Suède	Form. Formaldehyde ght Pen. Penetration Exh. Exhaustion

Table 44. Behavior of Different Dyes on Different Types of Leathers. BEHAVIOR ON POLLOWING STOCKS

Type of	Basic Basic Basic Basic Acid Acid Acid Acid Acid Acid Acid Cr. Acid	Direct Direct Direct Direct Direct Direct Direct Direct Direct Direct Direct Direct	Basic Basic	Acid Acid Acid Acid Acid Acid Acid Acid
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				Pr.
NAME OF DYE	CCCC Safranine Y Conc. CCCC Basic Red 4B Concacid Brilliant Scarlet 3B Conc. Comacid Brilliant Scarlet 3B Conc. Comacid Brilliant Scarlet 3B Conc. Comacid Red 4A Conc. Comacid Milling Red 3B Comacid Brilliant Scarlet 4R Comacid Brilliant Scarlet 4R Comacid Fruch B COCC Cfrome Red Bxtra	Trianol Direct Scarlet 3B Trianol Direct Scarlet B Trianol Direct Scarlet B Trianol Bast Red 8BL Trianol Bast Red 8BL Trianol Sarlet 4BS Trianol Rast Bordeaux G Trianol Rast Bordeaux G Trianol Bast Red 6B Trianol Bast Red 6B Trianol Developed Red 8B Trianol Developed Red 8B Trianol Developed Red 10B	CCCC Chrysoidine Y Extra Conc. CCCC Chrysoidine R Extra Conc.	Comacid Orange Y Conc. Comacid Orange 2R Conc. Comacid Fast Light Orange 2G Fastone Orange 4R Fastone Orange 4R Comacid Milling Orange G Comacid Milling Orange RN Comacid Milling Orange RN Comacid Milling Orange RN Comacid Milling Orange RR Comacid Milling Orange RR Comacid Milling Orange RR Comacid Milling Orange RR COCCC Alizarine Orange GR Trianol Orange R Special Trianol Orange R Special Trianol Orange R Special Trianol Orange SR

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BEHAVIOR ON FOLLOWING STOCKS

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Table 44.—(Concluded)
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In preparing Table 44, it was recognized that it is difficult to follow any rigid rule in comparing colors. If a color works well for a medium shade, it is marked good, even though it may not be suitable for light or pastel shades. The ratings for basic dyes are those for dyeing vegetable tanned leathers; they may not hold true for chrome-tanned stock mordanted with natural dyes. The ratings for syntan leathers are for leathers tanned with both chrome and syntans.

Mr. H. B. Marshall of Ciba Company, Inc. furnished the data given in Table 45. The dyes are separated according to kind and use to which they are to be put. With each dye is given the Color Index number to identify it with respect to the dyes of other manufacturers.

Books of color cards and procedures were also received from Calco Chemical Company and from National Aniline and Chemical Company, but these could not be

Table 45.	Dyes Used on Various Types of Leathers.
Basic Colors (used on vege	table sheep, and for topping on calf suède and splits.)
Color Index No. Name of Dye	Color Index No. Name of Dye
789 Phosphine GC	655 Auramine O 657 Malachite Green Crystals
789 Phosphine 2GC 332 Bismarck Brown R E 841 Safranine YN	xtra Conc. 749 Rhodamine B — Basic Black No. 2
909 New Blue RS Conc.	20 Chrysoidine Y
922 Methylene Blue 2B	
	rome side leather and chrome calf suède and spits.)
581 Direct Black EAC 581 Direct Black CX Do 406 Direct Blue 2B	uble — Direct Fast Bordeaux B Direct Violet N
406 Direct Blue 2B	420 Direct Brown MR Conc.
401 Melanthrene BHX 448 Benzopurpurine 4B	420 Direct Brown M. Conc. 561 Triazol Brown B
448 Benzopurpurine 4B 327 Direct Scarlet SE	596 Direct Brown 5C Extra Conc.
382 Direct Fast Red 3B 415 Direct Orange R	620 Direct Yellow TG Conc. 621 Direct Fast Orange 2R
419 Direct Fast Red F	021 Direct Past Grange 2R
Acid Colors (u	sed on side leather, calf, splits and sheep)
666 Acid Green	10 Napthol Yellow S
— Kiton Pure Blue A— Acid Blue RBF	146 Azo Yellow
208 Brilliant Acid Blue	R 151 Orange YZ R 161 Kiton Fast Orange 2R
Pr. 199 Victoria Fast Viole	t L. Conc. 234 Resorcine Brown B Extra Conc. 235 Resorcine Brown 3R Extra carlet MOO 289 Cloth Fast Blue R
698 Acid Violet 4BNS	Extra Conc. 235 Resorcine Brown 3R Extra
Conc.	— Leather Grey RC
176 Rocceline	- Fast Leather Brown EGC
262 Cloth Red 2B Conc 246 Acid Black BB Con	
- Acid Blue SM	138 Orange MNO
Neolan Colors (used on me	n's weight calf skins to produce a non-pigment finish.)
— Neolan Yellow BE	— Neolan Brown GC
 Neolan Yellow GR Pr. 146 Neolan Orange R 	Extra — Neolan Violet 5R — Neolan Violet R
— Neolan Orange G	Pr. 144 Neolan Blue 2G
— Neolan Red 3B	- Neolan Blue 2R
— Neolan Red GRE	- Neolan Navy Blue 2RL Conc.

Neolan Bordeaux R

Neolan Brown GR

Pr. 145

Neolan Green BL Conc.
 Pr. 143 Neolan Black WA Extra

reproduced properly in this book. However, they contain much information of great value to the leather dyer, which he can obtain directly from the manufacturers.

Natural Dyestuffs

Before the advent of the aniline dyestuffs, tanners were almost entirely dependent upon natural dyestuffs and vegetable tanning materials for their colors. Mr. H. R. Tisdale of American Dyewood Company has supplied books of color cards and procedures as well as the following list of vegetable materials used as dvestuffs:

Logwood (both oxidized and unoxidized) Fustic Hypernic Quercitron bark Osage orange wood Cutch (Burma) Cutch (Mangrove) Gambier (common, cube and plantation) Sicilian sumac leaves Domestic sumac

Gallnuts Divi divi Hemlock bark Valonea Myrobalans Wattle bark Chestnut wood Chestnut oak bark Ouebracho

Most of these have been described above and in preceding chapters. These natural vegetable materials play a big part in the dyeing of leather, usually for mordanting or providing the bottom color, and are often topped with aniline dyes. In many cases, they represent a considerable saving of money with an improved result.

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Chapter 16

Drying Light Leathers and Mechanical Operations

Proper drying and mechanical handling of leather are among the most vital operations in the tannery. Until comparatively recently, drying was generally considered as merely an incidental operation to be done as quickly and cheaply as possible without regard to changing conditions of the atmosphere and changing rates of drying. During rainy weather, a tanner might heat the air of a drying room to speed up drying or he might allow for a very much longer drying period. Often tanners dried their leather in drying tunnels equipped with fans to circulate the air and with heating coils to raise the temperature whenever the leather refused to dry at a reasonable rate. When the outside temperature was well below the freezing point, it was often found that the leather at room temperature dried so rapidly that it shrank to smaller area than usual and became rough and badly distorted in shape. The effects of this were partly overcome by dampening the leather after drying, flexing it by staking and then tacking it out on boards to dry again in a flat and extended condition.

There are so many different operations involved in making leather that often a tanner could not attribute to any one operation serious defects found in the finished leather, and the operation of drying seemed so simple that it was seldom suspected at all, even when it was the sole cause of the defects. Probably the advent of chrome tanning did more than any one thing to make tanners aware of the fact that improper drying conditions and improper mechanical handling of the stock during drying can completely ruin otherwise perfect leather.

Fifty years ago most light leathers were vegetable tanned, and tanners had become fairly well skilled in the drying and mechanical handling of such leathers without a knowledge of relative humidity of the atmosphere. In some tanneries the old methods are still in use without much change resulting from our growing knowledge of air conditioning.

Drying Vegetable-tanned Calf Leathers

After vegetable-tanned calf leathers have been fatliquored and colored and set out just as smoothly and completely as possible, each skin is laid out flat on a table, grain side up, and the grain surface is coated with oil. Various mixtures of oils may be used, but one found quite satisfactory consists of a mixture of 3 parts of denatured olive oil to 1 part of light paraffin oil. This oil retards the evaporation of water from the surface, preventing the drying from being too rapid and the tannins in the grain surface from oxidizing, which would discolor the leather. Instead of becoming brittle, the grain surface remains soft. The oiled skins are then laid out smoothly on wooden boards and held in place by tacks driven in close to and all around its outer edges, a few inches apart. This operation can be seen in detail in Fig. 300 of Chapter 15 (p. 479). In tacking the leather, the skins are not pulled out and extended more than is necessary to keep them flat and smooth. During the drying, the skin tends to shrink to some extent, but its area is maintained by the tacks, and the leather after drying is very smooth. In the

picture, the wooden frame is large enough so that two skins may be tacked onto each side of it, making four skins to the frame.

After the skins have been tacked onto a frame, the frame is stacked vertically with many other frames, as shown in the background of Fig. 300. The edges of the frames are so built up that there is a space of about three inches between the skins of one frame and those of the next frames. This is done to prevent skins from touching during drying and to allow sufficient space for ventilation. The frames are stacked on wooden rails to keep them several inches above the floor to allow complete circulation of air between the skins.

Above the frames are placed ordinary large fans which force a circulation of air between the frames. Where there is no temperature and humidity control of the air, a skilled foreman regulates the operation of the fans, the temperature of the air and the position of the frames with respect to the fans, so that the drying proceeds uniformly over a 24- to 48-hour period. In some plants today, the foreman is guided in his judgment also by frequent measurements of relative humidity. If by chance the speed of drying increased at such a rate as to cause oxidation and discolorations, the foreman would shut off the ventilating fans. The foreman learns by experience to draw the air either from the outside or from other departments of the tannery, and in this way exerts a rough control over both temperature and relative humidity, which may vary from 70° F. and 75 percent relative humidity at the start of the drying operation to 80° F. and 50 percent relative humidity at its conclusion.

When the leather is taken from the tacking frames, it usually contains about 10 to 12 percent by weight of water, which is considered air dry. At this stage, the leather may feel somewhat firm, but it is easily made soft and flexible by a light staking in the air-dry condition and it is then ready for finishing.

Drying Chrome-tanned Calf Leathers

When tanners who had previously tanned only vegetable-tanned calfskins first started to make chrome leather, they ran into many difficulties. The leather, after drying, was so hard and tinny that it could not be staked without damage to the leather. It was found necessary to dampen the leather with water and allow it to condition for a day or more before it could be staked and made flexible enough for use. Moreover, it was found that the tendency for the leather to shrink during drying was relatively enormous. Tacking out the leather on frames for drying prevented this shrinkage, but only by rupturing the fibers to such an extent as to make the finished leather very loose and pipey. After many failures, they found it best to hang the leather to dry so that it could shrink and dry without tension, and then to dampen it by piling it in damp sawdust for a day or more, stake it to make it flexible and then to tack it out for final drying.

This resulted in a loss of about 10 percent in area-yield of leather, but the leather was so improved in quality as more than to offset the loss in area. This method became practically universal and is still widely practiced. Tanners are employing drying tunnels to an ever increasing extent; this makes it easy to control rates of drying by controlling the rate of flow of air and its circulation through the stock, as well as the incoming and outgoing temperature and relative humidity of the air.

After the chrome-tanned skins have been set out after coloring and fatliquoring, they are hung to dry either in special drying rooms or by passing through specially designed drying tunnels. Fig. 325 shows the entrance to a modern drying tunnel; inside is a pair of endless-chain belts supporting many wooden beams equipped with

sharply pointed hooks. The operator hangs the skins from these hooks and they are taken off at the other end in a dry condition. Sometimes the skins are merely hung over poles or rods. Fig. 326 shows calfskins hung in this way after they have left the drying tunnel. At this stage, the dried leather is very hard and tinny.

To get a better appreciation of the cause of this hard condition, it would be well to refer back to the section of Chapter 15 headed "What Fatliquor Does to Leather." Here it was explained how and why the fibers of a skin cohere with enormous forces whenever they are allowed to dry from a wet state while in contact. These forces are lessened when the surfaces of the fibers are first coated with oil, as in fatliquoring. They are also lessened to a very marked degree by vegetable

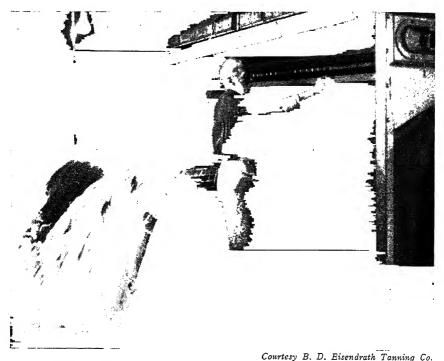


Fig. 325. Hanging Chrome-tanned Calfskins to Dry at the Entrance of Drying Tunnel.

tanning, but not by chrome tanning. In fatliquoring chrome-tanned calfskins, very much less oil is used than in the case of vegetable-tanned calfskins, with the result that the forces of cohesion of the fibers of the chrome-tanned leathers are vastly greater than for the vegetable-tanned leathers.

During the drying of the fibers which are in contact, a critical water content is reached at which the cohesions become effective. This water content has a value of about 34 percent. If the leather is examined when its water content has dropped to only about 35 percent, the fibers will be found not to be strongly cohering. But, as the water content is decreased below 34 percent, the fibers will be found to cohere with increasing vigor. When the leather has dried completely, it will be found that the fibers are cohering so strongly that any attempt to sep-

arate them by flexing will result in actual rupture of the fibers themselves. During the drying of chrome-tanned leather, it undergoes a considerable shrinkage in volume and this shrinkage is greatly increased by the cohesions of the fibers, the leather finally becoming very dense, hard and tinny.

Before the leather can be made to serve its normal purposes, it is necessary to reduce the number of cohesions of the fibers. Before the fibers can again be separated practically by flexing, it is necessary to dampen the leather with water back to a water content of about 34 percent. At this water content, the fibers can be separated by the flexing action of the staking machine without rupturing the fibers. When the fibers have been separated at this water content and the leather is then dried, the tendency for the fibers to cohere is greatly lessened and the leather dries out soft and flexible.

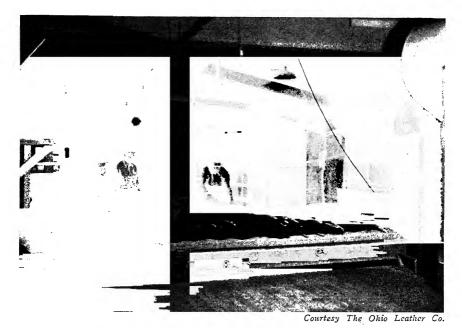


Fig. 326. Chrome-tanned Calfskins Coming from Drying Tunnel.

However, if the leather is staked when its water content is much above 34 percent, the fibers are readily separated but they again cohere strongly as the water content is decreased by drying to a point much below 34 percent. Thus the operation of dampening for staking requires delicate control. Unlike vegetable-tanned leather, chrome-tanned leather does not absorb water quickly, and it does not readily wet back to its condition before drying.

Dampening Chrome-tanned Leather for Staking

Without laboratory control, the dampening of chrome-tanned leather for staking requires considerable skill. One of the commonest practical methods involves packing the leather in dampened sawdust and leaving it there for a day or longer to absorb just the right amount of water, an operation known as *samming*. The

experienced operator adds water to sawdust and mixes it thoroughly. He judges the amount of water to add by the feel of the sawdust and determines when the leather packed in it is ready for staking by feeling it. All this requires a great deal of skill and experience. Laboratory control is much more time-consuming, but it does not require previous experience and is more reliable than the sense of feel of most operators.

If uniform results are to be obtained, it is necessary to control the drying operation so that the air-dry leather always contains the same amount of water, say 10 percent. It is convenient to make calculations on the basis of a pack of leather of 1000 lbs. air-dry weight. This pack will contain 900 lbs. of absolutely dry leather and 100 lbs. of water. A pile of sawdust is taken containing 750 lbs. of dry sawdust and 750 lbs. of water, intimately mixed. First a thin layer of damp sawdust is placed on the floor and then a skin is laid on it. Then a layer of sawdust is sprinkled over the skin and another skin is placed on it. This is continued until a pile is built containing the 1000 lbs. of air-dry leather and the 1500 lbs. of sawdust of 50 percent water content, the sawdust being evenly distributed



Fig. 327. Dipping Chrome-tanned Calfskins in Water Preparatory to Samming for Staking.

throughout the pile, which is then covered with a heavy canvas blanket and allowed to sam until the water is evenly distributed between sawdust and leather. Although the sawdust and leather do not have exactly the same affinities for water, any differences are too small to have any practical effect. At equilibrium,

we have 850 lbs. of water held by 1650 lbs. of dry leather and sawdust, giving both leather and sawdust an average water content of 34 percent. The time allowed for attainment of equilibrium is from 24 to 48 hours, and the temperature should be kept between 65 and 75° F. or as nearly within this range as is practical.



Courtesy The Ohio Leather Co.

Fig. 328. Crusting Chrome-tanned Calfskins.

Another common method of dampening leather for staking is either to dip it in water or to sponge it with water so that each 1000 lbs. of air-dry leather, receives 364 lbs. of water. The leather is then piled and covered to sam for a day. Fig. 327 shows a skilled operator dipping chrome-tanned calfskins into a tank of water preparatory to piling them for samming.

Some tanners dry their leathers very quickly to a water content much below 10 percent in which condition they do not wet back readily nor uniformly in samming. Before samming such leather, it is desirable to allow it to take up water from the air to attain a water content of about 10 percent. Upon being taken from the drying tunnels, the leather is simply piled in an open room and allowed to condition. It may be kept in the conditioning room for an indefinite period. This conditioning operation is known as *crusting*. Fig. 328 shows piles of chrome-tanned calfskins *in crust*.

Staking

When the skins are taken after samming at a uniform water content of about 34 percent, it is necessary to separate the fibers by a flexing action before the skins have had a chance to dry very much. This is done on a *staking machine*.

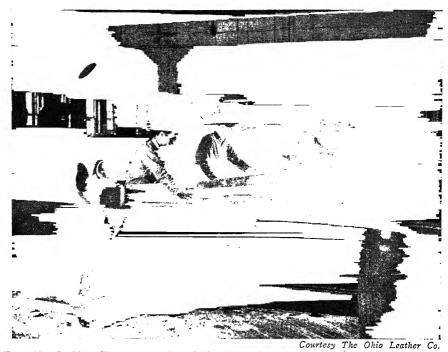


Fig. 329. Staking Chrome-tanned Calfskins After Samming and Before Tacking to Dry.



Fig. 329 shows a battery of staking machines with operators at work staking chrome-tanned calfskins. The operator in the foreground has just placed a calfskin on the table of the machine. The table is divided into two parts with an opening between them about 10 inches wide. The machine is equipped with two long jaws, one above and one below the table. The upper one has a rubber roll at its end and the lower one has a bladed opening into which the roll of the upper jaw may sink. The jaws are open as they come toward the operator, and he slides a portion of the skin between them. The jaws then come together and pull back. As they do so, they force the leather to flex sharply over the



Courtesy B. D. Eisendrath Tanning Co.

Fig. 331. Stakers at Work on Chrome-tanned Calfskins After Samming Before Drying.

blades of the lower jaw and around the roll of the upper jaw. With each such movement of the jaws, the operator shifts the position of the skin so that each portion of the area of the skin is flexed or staked by the moving jaws. The operator can regulate the pressure of the staking by the position of the blades of the lower jaw and the depth to which the upper roll forces the leather between the blades. Usually less pressure is applied over the flanks and looser parts of the skin. The operator holds the skin in place against the backward pull of the jaws, and some machines are equipped with automatic clamps that grip the skin when the jaws are staking it. Instead of a roll in the upper jaw, some machines have a smooth blade which forces the leather into a slot; both blade and slot pull backward with the leather between them, flexing the leather sharply along

their path. Fig. 330 shows a machine with the automatic clamp extending downward from the frame. Each time the jaws pull backward, staking the skin, the clamp grips the skin tightly and holds it to the operator's end of the table. These machines are usually equipped with a blade instead of a roll and are usually used for the second staking, which is done after drying and before finishing in order to break up slight cohesions between the fibers that still remain. This operation is often referred to as grain staking.

Fig. 331 shows another interesting view of stakers at work on chrome-tanned calfskins before tacking and drying.



Courtesy The Ohio Leather Co.

Fig. 332. Tacking Out Chrome-tanned Calfskins After Staking Before Drying.

Tacking or Toggling

After the skins have been staked and before they have had a chance to dry very much from their 34 percent water content, they are often tacked out on boards so that they will dry in a smooth and extended condition. Fig. 332 shows tackers at work on a calfskin taken immediately after staking. One skin is tacked onto each side of a wooden frame and the frames are stacked vertically under a revolving fan, much as in the case of vegetable-tanned calfskins.

Among the time and labor savers in modern drying systems are complete drying units consisting of perforated metal frames which slide into place, forming their own drying chamber. A frame slides out of its place in the unit in a horizontal direction, the frame itself being in a vertical position attached to a support so that it can be rotated. The frame is turned to a horizontal position and a skin is attached to it by means of toggles. A toggle is a metal clamp, capable of grip-

ping the leather along an edge, with a hook which can be inserted into one of the holes of the perforated frame. The workmen clamp toggles to the skin all along its outer edge and then pull the toggles away from the center and insert the hooks in the perforations in the frame so that the skin is pulled out smooth and tight. The frame is then rotated so that the opposite side is up, and a second skin is toggled onto it. The frame is then rotated to the vertical position and slid back into the drying unit. Fig. 333 shows three workmen toggling out a calfskin. Behind them a frame has been slid out of the drying unit to show a calfskin in the course of drying. Fig. 334 shows another such drying unit.

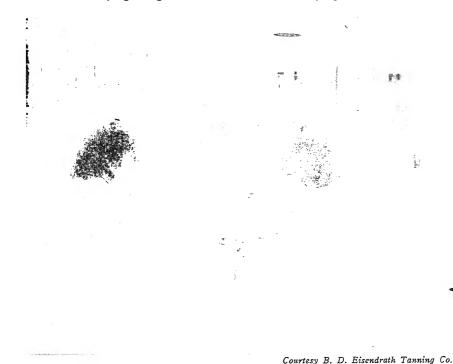


Fig. 333. Toggling Out Chrome-tanned Calfskins for Drying in Unit Dryer.

Each frame is so constructed that when all are in place, they form their own drying chamber, and conditioned air is circulated around and between the skins so that they dry completely in only a few hours. After the leather has been dried, it is taken off the frames and allowed to stand for a few hours or longer to take up a little moisture from the atmosphere; it is then dry-staked and sent to be finished.

Knee Staker

The simple knee staker was probably the forerunner of the modern staking machine, and it is still in use in some tanneries for staking very small skins and pieces of leather and for staking only small areas of larger skins. It derives its name from the fact that the workman uses his bare knee in operating it. The workman wears a pair of trousers with one leg cut off above the knee.

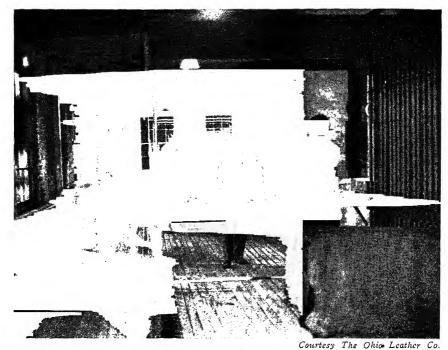


Fig. 334. Toggling Chrome-tanned Calfskins.

knee staker consists simply of a rounded metal blade set in a heavy squared log, as shown in Fig. 335. The workman presses the leather against one side of the blade with his bare knee and with his hands pulls the leather sharply across the blade with a pressure varying according to the amount of flexing required to soften the leather without distorting it.

Air Conditioning

Air conditioning consists essentially of adjusting the temperature and water content of air to serve best some particular purpose. It is of very great economic importance to the tanner to have a thorough knowledge of the principles involved in air conditioning. It will not only enable him to save money in drying his leather, but it will help him to produce leather of higher quality. The properties of leather vary with the relative humidity of the atmosphere, and it is important to know in what manner and to what extent.

Solubility of Water in Air

At any given temperature, water has a limited solubility in air; that is, a given amount of air can dissolve or absorb only a fixed amount of water and no more. When air contains this limited amount of water, it is said to be saturated, and no wet material placed in it will dry or lose any water because saturated air contains all the water it can hold. However, the amount of water that air can hold increases with temperature. For example, if we analyze 1000 cu. ft. of saturated air at 100° F, we find that it contains exactly 2.851 lbs. of water and cannot

absorb any more. If we take 1000 cu. ft. of saturated air at 200° F., we find that it contains 29.700 lbs. of water. With each increase in temperature, the solubility of water in air increases.

When air is heated, it expands. For example 1000 cu. ft. of dry air at 70° F. weighs 74.92 lbs., but when heated to 200° F. it increases in volume to 1246 cu. ft., but still weighs 74.92 lbs. Thus when we refer to 1000 cu. ft. of dry air at 70° F., we refer to 74.92 lbs. of air, but when we refer to 1000 cu. ft. of air at 200° F., we refer to only 55.14 lbs. of air. This should be kept in mind in what

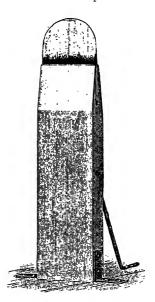


Fig. 335. Stehling Knee Staker.

Courtesy Chas. H. Stehling Co.

follows or confusion of ideas may result. Table 46 shows the total weights of both dry air and of water contained in 1000 cu. ft. of saturated air at different temperatures.

Table 46. Weights of Water and of Dry Air in 1000 Cu. Ft. of Saturated Air at Different Temperatures.

		ht in 1000 C		_	Wei	ght in 1000 C	u. Ft. —
Temp. (°F.)	lbs. Total	lbs. Water	lbs. Dry Air	Temp.	lbs. Total	lbs. Water	lbs. Dry Air
0	86.29	0.07	86.22	120	65.48	4.91	60.57
1Ŏ	84.42	0.11	84.31	130	63.46	6.34	57.12
20	82.62	0.18	82.44	140	61.29	8.12	53.17
30	80.88	0.28	80.60	150	58.91	10.28	48.63
40	79.17	0.41	<i>7</i> 8.76	160	56.31	12.92	43.39
50	<i>77.</i> 51	0.59	76.92	170	53.42	16.09	37.33
60	<i>75.</i> 86	0.83	75.03	180	50.22	19.89	30.33
<i>7</i> 0	74.22	1.15	73.07	190	46.66	24.38	22.28
80	72.57	1.58	70.99	200	42.68	29.70	12.98
90	70.90	2.13	68.77	210	36.16	35.93	2.30
100	69.19	2.85	66.34	212	37.29	37.29	0.00
110	67.37	3.76	63.61				

As the temperature increases, it will be noted that the proportion of water to dry air increases until at the boiling point of water, 212° F., the air consists

entirely of gaseous water. Fig. 336 shows the number of lbs. of water contained in 1000 cu. ft. of saturated air at different temperatures. This is an extremely valuable chart for the tanner because with it and a few simple instruments he can control the rate of drying of his leather.

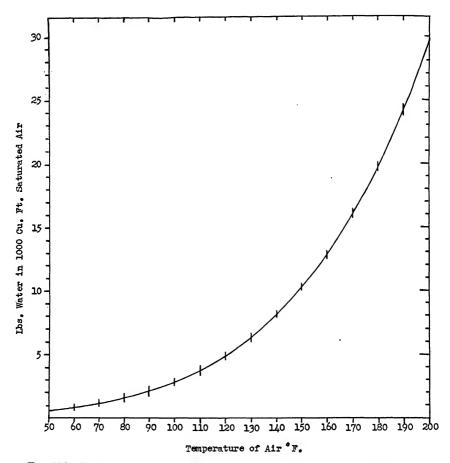


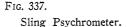
Fig. 336. Pounds of Water in 1000 Cubic Feet of Saturated Air at Different Temperatures.

Relative Humidity

When air is saturated with water, it cannot absorb any more and is said to have a relative humidity of 100 percent. When air is absolutely dry, it contains no water and is said to have a relative humidity of 0 percent. When air contains x percent as much water as an equal volume of saturated air, it is said to have a relative humidity of x percent. For example, suppose we measured the temperature and relative humidity of some air and found it to have a temperature of 70° F. and a relative humidity of 50 percent. By looking at Table 46 or Fig. 336, we would find that 1000 cu. ft. of saturated air at 70° F. contains

1.15 lbs. of water. We would at once know that 1000 cu. ft. of the air we had measured contained 50 percent of 1.15 lbs. or 0.575 lb. of water.

In Chapter 1, under the heading Glands and the Thermostat Mechanism, it was pointed out that a very large amount of heat is required to convert liquid water into gaseous water, without changing its temperature. If liquid water is brought into contact with unsaturated air, it will evaporate so long as the air above it remains unsaturated, even though no heat is applied to it. However, it must have additional heat to evaporate and so it simply takes it from its surroundings. Use is made of this fact in order to determine the relative humidity of air. If we wrap a tiny piece of cloth around the bulb of a thermometer, soak the cloth with water and place it in a current of air, any evaporation of water from the cloth will result in a lowering of the temperature of the wet cloth and of the bulb of the thermometer. The temperature reading of the thermometer will then be lower than that of the air. The lower the relative humidity of the air, the greater will be the rate of evaporation of water from the cloth and the bulb of





Courtesy Taylor Instrument Cos.

the thermometer and the lower will be the reading of the thermometer. If the cloth is kept wet and air is blown over it, the temperature reading will decrease to a low limit and then not decrease any further no matter how long the air is blown over it. It has been found that this lowering of the temperature is actually an accurate measure of the relative humidity of the air.

Relative humidity is usually measured by means of a hygrometer consisting of two thermometers, one of which has its bulb covered by a wick kept wet with water. Hygrometers are of many forms, but all work on the same basic principle. Fig. 337 shows the popular sling psychrometer used where one instrument is used to measure the relative humidity in different departments. The lower thermometer has a silk or cotton wick surrounding the bulb. When ready to make a determination, the operator dips the wick in water to wet it and then firmly holding

the handle, with the psychrometer dangling from it at the end of the chain, he swings the psychrometer in a circulatory motion, stopping at intervals of about one minute to read the wet-bulb thermometer. When this reading reaches its lowest point, he records the readings of both wet-bulb and dry-bulb thermometers. From these two readings, he finds the relative humidity in the Relative Humidity Tables.

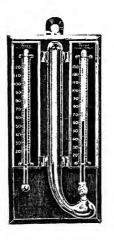


Fig. 338.

Mason's Form of Wall Hygrometer.

Courtesy Taylor Instrument Cos.

Fig. 338 shows Mason's form of wall hygrometer. Between the wet-bulb and dry-bulb thermometers, there is a reservoir tube filled with water which is curved at the bottom, terminating in an open cup. A wick placed over the bulb of the wet-bulb thermometer has one end dipping into the cup of water so that it is kept wet at all times. A fan is so placed that it blows a continuous current of air across the wet bulb. As long as the reservoir is kept filled with water, the wick is clean and air is blowing across it, the wet-bulb and dry-bulb temperatures can be read at any time without waiting.

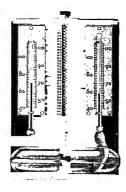


Fig. 339.

Mason's Form of Humidiguide.

Courtesy Taylor Instrument Cos.

Fig. 339 shows Mason's form of humidiguide. This is similar to the wall hygrometer, but it has a rotating cylinder between the two thermometers from which the relative humidity can be read from the readings of the wet-blub and dry-bulb thermometer without referring to the Relative Humidity Tables.

Fig. 340 shows a Taylor hygrometer for continuous recording of the wetbulb and dry-bulb temperatures. With one of these placed at both the inlet and outlet ends of the drying tunnel, an operator can readily make adjustments of temperature and air flow to increase the efficiency of the drying. Equipment is also available for automatically controlling relative humidity.

When the wet-bulb and dry-bulb temperatures are both known, the relative humidity can be found in the Relative Humidity Tables given in Table 47, which are taken with permission from the Relative Humidity Tables prepared by Taylor Instrument Companies, Rochester, New York.

In submitting the data given in Table 47, the Taylor Instrument Companies issued the following foreword: "These tables are computed from data supplied by the Bureau of Standards and are correct at a barometric pressure of 29.92. At lower barometric pressures, the tables are slightly in error. At 25.00 inches barometric pressure at normal air temperature, the error is minus 1 percent at 90

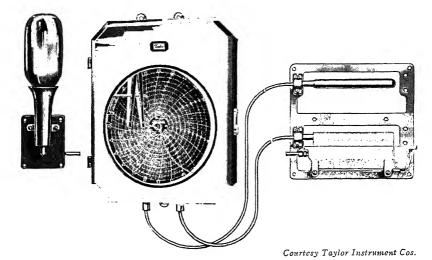


Fig. 340. Wet-and-Dry-Bulb Recording Hygrometer.

percent relative humidity and minus 5 percent at 20 percent relative humidity. This error diminishes slightly with rise and increases slightly with fall in air temperatures. It is cautioned that values above 140° dry bulb are extrapolated. Should complete tables covering barometric pressure be desired, apply to the superintendent of documents, Government Printing Office, Washington, D. C. for psychrometric tables WB-235." It is also pointed out that the values in the tables are for air velocity of not less than 600 ft. per minute. Care should be taken to keep the wick on the wet-bulb thermometer clean. It should not be handled unless the fingers are perfectly clean. Distilled water should be used. If the wick becomes hard (which can easily be detected by feeling it), it should be discarded and replaced by a new one.

How to Use the Tables

In order to get the value for percent relative humidity of the air, it is necessary to have both the wet-bulb temperature and the dry-bulb temperature. Increasing

(Text cont'd on page 539)

Table 47. Relative Humidity of Air as a Function of Wet-bulb and Dry-bulb Temperatures.

D										Te	emp	era	ture	s.									
Dry- bulb	_									·We	t-bı	ılb I	Гетр	erat	ure (°F.)							
Temp. (°F)	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50
40	7	15	22	29	37	45	52	60	68	75	83	92	100										
41	3	10	17	24	31	39	46	54	61	69	76	84	92	100									
42	Ť	5	12	19	26	33	40	47	55	62	69	77	85	92	100								
43	•	•	8	14	21	28	35	42	48	55	63	70	77	85	92	100							
44	•	•	4	10	16	23	30	36	43	49	56	63	71	78	85	93	100				٠		
	•	•	4		12		23	31	38	44	51	57	64	71	78	86	93	100					
45	•	٠	•	6		18						52	58	65	72	79	86	93	100				
46	٠		•	•	8	14	20	26	32	39	45				-		79	86		100			
47	•	•	•	•	5	10	16	22	28	34	40	46	52	59	66	72			93				
48	٠	٠	٠	•	1	7	12	18	23	29	35	41	47	54	60	66	73	79	86	93	100		
49	•	•	•	٠	•	3	9	14	19	25	31	36	42	48	54	61	67	73	80	86	93	100	
50	٠	•	٠	٠	•	•	5	10	16	21	27	32	38	43	49	55	61	67	74	80	87	93	100
51		٠		٠	•	•	•	7	12	17	23	28	34	39	45	50	56	62	68	75	81	87	94
52				٠	•			4	9	14	19	24	29	35	40	46	51	57	63	69	75	81	87
53				•	•	٠		1	б	10	16	20	26	31	36	41	47	52	58	63	69	75	81
54									3	8	12	17	22	27	32	37	42	48	53	59	64	70	76
55										5	9	14	19	23	28	33	38	43	49	54	59	65	70
56										2	7	11	16	20	25	30	34	39	44	50	55	60	65
57											4	8	13	17	22	26	31	35	40	45	50	55	61
58											1	6	10	14	18	23	27	32	37	41	46	51	5 6
59												3	7	11	16	20	24	29	33	38	42	47	52
60												1	5	9	13	17	21	26	30	34	39	43	48
61														7	10	14	18	22	27	31	35	40	44
62														4	8	12	16	20	24	28	32	36	41
63														2	6	10	13	17	21	25	29	33	37
64															4	7	11	15	18	22	26	30	34
65															2	5	9	12	16	20	24	27	31
66								,								3	7	10	14	17	21	25	29
67							•	•	•	•	•		•	•		2	5	8	12	15	19	22	26
68		٠	•	•	٠	•	٠	٠	•	•	•	•	•		•	٠	3	6	10	13	16	20	23
69	٠	٠	•		•	•	•	•	•	•	•	•	•	•	•	•	1	5	8	11	14	18	21
70	•	٠	٠	•	•	•	•	٠	٠	•	•		٠	•	•	•	٠	3	6	9	12	15	19
71	•	•	•	•	•	•	•	•	•	•	•	٠	•	٠	٠	•	٠	1	4	7	10	13	17
72	•	•	•	٠	٠	•	•	•	•	•	•	٠	•	•	٠	٠	٠	٠	3	6	9	12	15
73	•	•	•	•	•	٠	•	•	•	•	•	٠	٠	•	•	•	•	•	1	4	7	10	13
74	•	•	•	•	٠	•	•	٠	٠	•	•	٠	•	•	•	•	•	•	٠	3	5	8	11
75 76	•	•	•	•	•	•	•	•	•	•	•	•	•	٠	•	•	•	•	•	1	4	7	9
76 77	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	٠	•	•	•	3	5	8
78	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	1	4	6
79	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	3	5
80	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	1	4
30	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	٠	•	•	•	•		3

Table 47.—(Continued)

Dry-	Table 47.—(Continued) Wet-bulb Temperature (°F.)																					
bulb	~							— V	Vet-	bulb	Tem	pera	ture	(°F.)							$\overline{}$
Temp. (°F.)	51	52	5 3	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72
51	100																					
52	94	100																				
53	87	94	100																			
54	82	88	94	100																		
55	76	82	88	94	100	***																
56 57	71	76 71	82 77	88 82	94 88	100 94	100															
57 58	66 61	66	72	77	83	88	94	100														
59	57	62	67	72	78	83	89	94	100													
60	53	58	63	68	73	78	83	89	94	100												
61	49	54	58	63	68	73	78	84	89	94	100											
62	45	50	54	59	б4	69	74	79	84	89	94	100										
63	42	46	50	55	60	64	69	74	79	84	89	95	100									
64	38	43	47	51	56	60	65	70	74	79	84	90	95	100								
65	. 35	39	44	48	52	56	61	66	70	75	80	85	90	95	100		•					
66	32	36	40	44	48	53	57	61	66	71	75	80	85	90	95	100						
67	30	33	37	41	45	49	53	58	62	66	71	75	80	85	90	95	100					
68	25	31	34	38	42	46	50	54	58	62	67	71	76	80	85	90	95	100	100			
69	24	28	32	35	39	43	47	51	55	59	63	67	72	76	81	85	90	95	100	100		
70	22	25	29	33 30	36	40 37	44 41	48 45	51 48	55 52	59	64 60	68 64	72 68	77 72	81 77	86 81	90 86	95 90	100 95	100	
71 72	20 [°] 18	23 21	27 24	28	33 31	34	38	42	48	32 49	56 53	57	61	65	72 69	73	77	82	86	91	95	100
72	16	19	22	25	29	32	35	39	42	46	50	53	57	61	65	69	73	78	82	86	91	95
74	14	17	20	23	26	29	33	36	39	43	47	50	54	58	61	65	69	74	78	82	86	91
75	12	15	18	21	24	27	30	34	37	40	44	47	51	54	58	62	66	70	74	78	82	86
76	11	13	16	19	22	25	28	31	34	38	41	44	48	51	55	59	62	66	70	74	78	82
77	9	12	14	17	20	23	26	29	32	35	39	42	45	48	52	56	59	63	67	71	74	79
78	8	10	13	16	18	21	24	27	30	33	36	39	43	46	49	53	56	60	63	67	71	75
79	6	9	11	14	17	19	22	25	28	31	34	37	40	43	46	50	53	57	60	64	68	71
80	5	7	10	12	15	18	20	23	26	29	32	35	38	41	44	47	50	54	57	61	64	68
82	2	4	7	10	12	14	17	20	23	25	28	30	33	36	39	42	45	48	52	55	59	61
84	•	2	5	7	10	12	14	16	19	21	24	26	29	32 28	35	37 33	40 36	43 39	46 42	49 44	52 47	56 50
86	•	•	3 1	5 3	7 5	9 7	12 9	14 11	16 13	18 15	21 18	23 20	26 23	28 25	31 28	30	33	35	38	40	43	46
88 90	•	•	1	1	3	5	7	9	11	13	15	17	20	22	24	26	29	31	34	36	38	41
92	•	•	•	•	1	3	5	7	9	11	13	15	18	19	21	23	26	28	30	32	34	37.
94	•					1	3	5	7	9	11	12	14	16	18	20	22	24	27	29	31	33
96							1	3	5	7	9	10	12	14	16	18	20	22	24	26	28	30
98								1	3	5	7	8	10	12	14	15	17	19	21	23	25	27
100									1	3	5	7	8	10	11	13	15	17	19	21	23	24
102	•	٠	•	•	•	٠	•	•	•	1	3	5	7	8	9	11	13	15	17	18	20	22
104 106	•		•	•	•	•	:	:	•	•	1	3 1	5 3	7 5	8 7	10 8	12 10	13 11	15 13	16 14	18 15	20 17
108	·				Ċ								1	3	5	7	9	10	11	12	14	16
110														1	3	5	7	8	9	11	12	14
112					•	•	•	•	٠	•	•		•	•	1	3	5	7	8	9	10	12
114	•		•	•	٠	•	•	•	•	•	•	•	•	•	٠	1	3	6	7	8	9	11
116 118		•	•	•	٠	•	•	•	•	•	•	•	•	•	•	:	1	3 1	5 3	6 5	7 6	9 8
120		•		:		:	:	:	•	:	•		•	:		•					4	6
	•		•	•	•	-	-	-	-	-	•	-	-									

Table 47.—(Continued)

Dev						Tab	le 47	' .—(Con	inue	d)							
Dry- bulb							-Wet	-bulb	Tem	perati	are (°	F.) –						
Temp. (°F.)	74	76	78	80	82	84	86	88	90	92	94	96	98	100	102	104	106	108
74	100																	
76	91	100																
78	83	91	100															
80	75	83	91	100														
82	69	76	84	92	100													
84	62	69	76	84	92	100												
86	57	63	70	77	84	92	100											
88	51	57	64	70	77	85	92	100										
90	47	52	58	65	71	78	85	92	100									
92	42	48	53	59	65	72	78	85	92	100								
94	38	43	49	54	60	66	72	79	85	93	100							
96	35	39	44	50	55	61	66	73	79	86	93	100						
98	32	36	40	45	50	55	61	67	73	79	86	93	100					
100	28	33	37	41	46	51	56	62	68	73	80	86	93	100				
102	26	30	34	38	42	47	52	57	62	68	74	80	86	93	100			
104	23	27	31	35	39	43	48	53	58	63	69	74	80	87	93	100		
106	21	24	28	32	36	40	44	49	53	58	64	69	75	81	87	93	100	
108	19	22	25	29	33	37	41	45	49	54	59	64	70	75	81	87	93	100
110	17	20	23	26	30	34	38	42	46	50	55	60	65	70	75	81	87	93
112	15	18	21	24	27	31	35	38	42	47	51	55	60	65	70	76	81	87
114	13	16	19	22	25	28	32	35	39	43	47	52	56	61	66	71	76	82
116	12	14	17	20	23	26	29	33	36	40	44	48	52	5 7	61	66	71	76
118	11	13	16	18	21	24	27	30	34	37	41	45	49	53	57	62	67	72
120	9	12	14	1 <i>7</i>	19	22	25	28	31	34	38	41	45	49	5 3	58	62	67
122	8	10	13	15	18	20	23	2 6	29	32	35	39	42	46	50	54	58	63
124	٠	9	11	14	16	18	21	24	27	30	33	36	39	43	47	50	54	59
126	•	8	10	12	15	17	19	22	25	27	30	33	37	40	44	47	51	55
128	•	٠	9	11	13	16	18	20	23	25	28	31	34	37	41	44	48	52
130		•	•	10	12	14	16	19	21	24	26	29	32	35	38	41	45	48
132 134	•	•	•	•	11	13	15	17	20	21	24	26	30	33	36	39	42	45
136	•	•	•	•	•	12	14 13	16 15	18 17	20 19	22 21	25 23	27 26	30 28	33 31	36 24	39	43
138	•	•	•	•	•			14	15	17	20	22	24	27	29	34 32	37 34	40 37
140	·		·	•	•	•		•	14	16	18	21	23	25	27	30	32	35
142	·	Ċ				·	•		• •	15	18	20	22	24	26	28	31	33
144											16	19	21	23	25	27	29	31
146				-								16	19	21	23	25	27	29
148													17	20	22	24	26	28
150														18	21	23	25	27
152															18	21	23	25
154																19	22	24
156					•					•	•						19	22
158					٠												,	20

Table 47.—(Continued)

D						Tab	le 47	7.—(Cont	inue	d)							
Dry- bulb							-Wet	-bulb	Tem	perati	ıre (°	F.) —						
Temp. (°F.)	110	112	114	116	118	120	122	124	126	128	130	132	134	136	138	140	142	144
110	100																	
112	94	100																
114	88	94	100															
116	82	88	94	100														
118	77	82	88	94	100													
120	72	77	82	88	94	100												
122	67	72	77	83	88	94	100											
124	63	68	73	78	83	88	94	100										
126	59	64	68	73	78 72	83	88	94	100	100								
128 130	56	60	64 60	68	73	78	83	89	94	100	100							
132	52 49	56 53	60 56	64 61	69 65	73 69	78 74	83 79	89 84	94 89	100 94	100						
134	46	49	53	57	61	65	69	74	79	84	89	94	100					
136	43	46	50	54	57	61	65	70	74	79	84	89	94	100				
138	40	44	47	50	54	58	62	66	70	75	79	84	89	94	100			
140	38	41	44	47	51	54	58	62	66	70	75	79	84	89	95	100		
142	36	39	42	45	48	52	5 5	59	63	67	71	75	80	84	90	95	100	
144	34	36	39	42	45	48	52	55	59	63	67	71	75	80	84	90	95	100
146	32	34	37	40	43	46	49	53	55	59	63	67	71	76	80	85	90	95
148	30	32	35	37	40	43	46	49	53	56	60	64	68	71	7 6	80	85	90
150	28	30	33	35	38	41	43	46	49	53	56	60	64	68	71	76	80	8 5
152	27	29	31	34	36	38	41	44	47	50	54	57	60	64	68	72	76	81
154	26	28	30	32	34	36	39	42	44	47	50	54	57	61	65	69	72	76
156	24	26	28	30	32	35	37	39	42	45	47	50	54	57	61	65	69	72
158	23	25	27	29	31	33	35	38	40	43	45	48	51	55	57	61	65	69
160	•	23	25	27	29	31	33	35	38	40	43	46	48	51	55	58	62	65
162	•	22	24	26	28	30	32	34	36	39	41	44	47	49	51	55	58	62
164	•	•	22	24 23	27 25	29 27	31 29	32 31	34	37	39 37	41 40	44 42	47 45	49 48	52 50	56 53	58 56
166	•	•	•						33	35								
168	•	•	•	•	23	25	27	29	31	33	35	38		42	45	48	50	53
170	•			•	•	23	25	27	29	31	33	35	38	40	42	45	48	50
172	•	•	•	•	•	•	24	26	28	30	32	34	36	39	41	43	46	49
174	•	•		•	•	•	•	24	26	28	30	32	34	36	39	41	43	46
176	•		•	•	•	•	•	•	25	27	29	31	33	35	37	40	42	44
178	•	•	•	•	•	•	•	•	•	25	27	29	31	33	35	37	40	42
180	•	•	•	•	•	•	•	•	•	•	26	28	30	31	33	35	37	40
182	•	٠	•	•		•	-		•	•	•	26	28	30	32	34	36	38
184	•		•			•	•		•		•	•	26	28	30	32	34	36
186		•		•			•		•		٠	•	•	27	28	30	32	34
188		-		•	•	•	•	•		•	•	•		•	27	29	31	33
190			•			•	•	•	•	•	•	•		•	•	2 8	30	32
192					•	•										•	28	30
194																	-	29

Table 47.—(Continued)

								•			•							
Dry- bulb	Wet-bulb Temperature (°F.) ————————————————————————————————————																	
Temp.(°F)	146	148	150	152	154	156	158	160	162	164	166	168	170	172	1/4	1/0	178	180
146	100	420																
148	95	100																
150	90	95	100															
152	85	90	95	100														
154	81	85	90	95	100													
156	77	81	85	90	95	100												
158	72	77	81	85	90	95	100											
160	69	73	77	81	85	90	95	100										
162	66	70	73	77	82	86	91	95	100									
164	62	66	70	73	78	82	86	91	95	100							,	
166	59	63	66	70	74	78	82	8 6	91	96	100							
168	57	59	63	67	70	74	78	82	. 86	91	96	100						
170	53	57	60	63	67	70	74	78	82	86	91	96	100					
172	51	54	58	60	63	67	71	74	79	83	87	92	96	100				
174	49	51	54	58	61	64	67	71	74	79	83	87	92	96	100			
176	47	50	52	55	58	61	64	68	71	75	79	83	87	92	96	100		
178	44	47	50	52	55	58	61	64	68	72	75	79	83	87	92	96	100	
180	42	44	47	50	52	55	58	61	64	68	72	75	79	83	87	92	96	100
182	41	43	45	48	50	53	56	5 9	62	65	69	72	76	79	83	87	92	96
184	38	41	43	45	48	50	53	56	59	62	65	69	72	7 6	79	83	87	92
186	37	39	42	44	46	48	51	54	57	60	63	66	69	73	76	80	83	87
188	35	37	39	42	44	46	48	51	54	57	60	63	66	69	73	76	80	83
190	33	35	37	39	42	44	46	49	51	54	57	60	63	66	69	73	76	80
192	32	34	36	38	40	42	44	47	49	52	.55	58	61	63	67	70	73	76
194	31	33	34	36	38	40	42	45	47	50	52	55	58	61	63	67	70	73
196	29	31	33	35	37	39	40	43	45	47	50	53	55	58	61	64	67	70
198		30	32	34	35	37	39	41	43	45	48	50	53	55	58	61	64	67
200		٠	30	32	34	36	38	40	42	44	46	48	51	53	56	59	62	65
202				30	32	34	36	38	40	42	45	47	49	52	54	57	60	63
204					30	32	34	36	38	40	42	45	47	49	52	55	58	60
206			٠.		29	31	33	35	37	39	41	43	45	48	50	53	55	58
208						30	32	33	35	37	39	42	44	46	48	50	53	55
210							30	32	34	36	38	40	42	44	46	48	50	53
212								31	33	34	36	38	40	42	44	46	48	51

Table 47.—(Concluded)

Wet-bulb Temperature (°F.)															
182	184	186	188	190	192	194	196	198	200	202	204	206	208	210	212
100															
96	100														
92	96	100													
87	92	96	100												
83	87	92	96	100											
80	84	88	92	96	100										
76	80	84	88	92	96	100									
74	77	80	84	88	92	96	100								
70	74	77	80	84	88	92	96	100							
68	72	75	78	80	84	88	92	96	100						
66	69	72	75	78	81	85	89	92	96	100					
63	66	69	72	75	78	81	86	89	92	96	100				
60	63	66	70	73	76	79	82	86	90	93	96	100			
58	61	64	67	70	73	76	79	82	86	90	93	96	100		
56	58	61	64	67	70	73	76	79	82	86	90	93	96	100	
54	56	58	61	64	67	70	73	77	79	83	86	90	93	96	100
	100 96 92 87 83 80 76 74 70 68 66 63 60 58	100 96 100 92 96 87 92 83 87 80 84 76 80 74 77 70 74 68 72 66 69 63 66 60 63 58 61 56 58	100 96 100 92 96 100 87 92 96 83 87 92 80 84 88 76 80 84 74 77 80 70 74 77 68 72 75 66 69 72 63 66 69 60 63 66 58 61 64 56 58 61	100 96 100 92 96 100 87 92 96 100 83 87 92 96 80 84 88 92 76 80 84 88 74 77 80 84 70 74 77 80 68 72 75 78 66 69 72 75 63 66 69 72 60 63 66 70 58 61 64 67 56 58 61 64	182 184 186 188 190 100	182 184 186 188 190 192 100	182 184 186 188 190 192 194 100	182 184 186 188 190 192 194 196 100 100 56 100 56 100 56 56 56 56 100 56 56 56 56 56 56 56 56 56 56 57 56 57	182 184 186 188 190 192 194 196 198 100	182 184 186 188 190 192 194 196 198 200 100 96 100 87 92 96 100 88 92 96 100 88 92 96 100 80 84 88 92 96 100 96	182 184 186 188 190 192 194 196 198 200 202 100 96 100 87 92 96 100 88 92 96 100 88 92 96 100 88 92 96 100 89 100 80 100 89 100	182 184 186 188 190 192 194 196 198 200 202 204 100 56 100 56 100 56 100 56 100 56 100 56 100 56 100 56 56 100 56 56 56 70 77 80 84 88 92 96 100 56 56 72 75 78 80 84 88 92 96 100 56 56 72 75 78 80 84 88 92 96 100 56 56 56 56 72 75 78 80 84 88 92 96 100 56 56 56 72 75 78 80 84 88 92 96 100 56 56 66 69 72 75 78 81 85 89 92 <t< th=""><th>182 184 186 188 190 192 194 196 198 200 202 204 206 100 96 100 56 100 56 100 56 100 56 100 56 100 56 56 56 56 56 66 67 70 73 76 79 82 96 100 56 57 78 80 100 56 58 66 69 72 75 78 80 84 88 92 96 100 56 56 70 73 76 70 7</th><th>182 184 186 188 190 192 194 196 198 200 202 204 206 208 100 56 100 56 100 56 100 56 100 56 100 56 56 100 56 56 100 56 56 100 56 56 100 56 56 570 78 80 100 56 56 56 100 56 56 56 56 570 78 100 56 56 56 56 570 78</th><th>182 184 186 188 190 192 194 196 198 200 202 204 206 208 210 100</th></t<>	182 184 186 188 190 192 194 196 198 200 202 204 206 100 96 100 56 100 56 100 56 100 56 100 56 100 56 56 56 56 56 66 67 70 73 76 79 82 96 100 56 57 78 80 100 56 58 66 69 72 75 78 80 84 88 92 96 100 56 56 70 73 76 70 7	182 184 186 188 190 192 194 196 198 200 202 204 206 208 100 56 100 56 100 56 100 56 100 56 100 56 56 100 56 56 100 56 56 100 56 56 100 56 56 570 78 80 100 56 56 56 100 56 56 56 56 570 78 100 56 56 56 56 570 78	182 184 186 188 190 192 194 196 198 200 202 204 206 208 210 100

values of wet-bulb temperatures are to be found running across the top of the tables on all 6 pages. First locate the wet-bulb temperature and then follow down the column which it heads until it intersects the column headed at the left by the dry-bulb temperature. The figure at the intersection of the columns is the percent relative humidity of the air. For example, suppose the wet-bulb temperature was found to be 98° F., when the dry-bulb temperature was 102° F. We find the wet-bulb temperature of 98° F. heading the 13th column of the third page of tables. Then at the left of the page we find the dry-bulb temperature of 102° F. heading the 15th column reading from left to right. Where the 2 columns intersect, we find the number 86, indicating that the air has a relative humidity of 86 percent.

The wet-bulb temperatures appear at intervals of 1° from 28° to 72° and at intervals of 2° from 72° to 212°. The dry-bulb temperatures appear at intervals of 1° from 40° to 80° and at intervals of 2° from 80° to 212°. This was done simply to conserve space in the tables. At the higher temperatures, where a temperature reading is an odd number, simply take the average of values for the next preceding and succeeding even numbers.

The Anemometer

An anemometer is a delicate instrument used to measure wind velocities and one is shown in Fig. 341. The construction principle embodies a windmill whose motion is communicated by suitable gearing to series of pointers moving over graduated dials. When it is placed in a current of air, the delicate windmill set in jewelled bearings spins, and the dials indicate the number of *linear feet* of air passing through the anemometer. The number of linear feet of air passing through in one minute gives the *velocity* of the air in *linear feet* per minute. If all the air entering or leaving a drying tunnel is forced to travel through a pipe having a cross-section area of 1 square foot, and the anemometer is set in this pipe, it will register in any given length of time the number of *cubic feet* of air that has passed

through the tunnel in that length of time. For a cross-section area of any other size, it is merely necessary to multiply the reading by the number of square feet of cross-section to get the number of cubic feet of air that has passed through the tunnel.

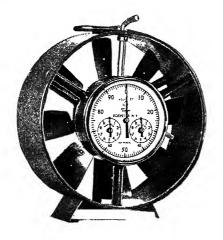


Fig. 341.

Courtesy Taylor Instrument Cos.

An Innovation in Preparing Leather for Staking

After fatliquoring and coloring chrome-tanned leather, it is customary to dry it out and then to dampen it back to a water content of about 34 percent for staking. Both the initial drying and the redampening must be done with reasonable precision, or else the properties of the leather may be greatly impaired. For the best results, this requires control of two separate operations, drying and redampening. In the initial drying, the fibers become glued together and then the cohesions are broken by redampening and staking.

It appeared possible to the writer to carry the initial drying of the leather only to the point where it contains 34 percent of water and then to stake it, thereby eliminating the initial complete drying operation and the redampening operation. This involved two serious problems: first determining the point in the initial drying where the water content of the leather was reduced to just 34 percent and then conducting this partial drying so that the 34 percent of water was uniformly distributed throughout the leather. The thinner parts of leather present more surface area per pound of leather and thus lose more water per unit of drying time than the thicker parts; thus, when an average water content of 34 percent is reached, the water in the leather is not uniformly distributed. The thicker parts contain more water than the thinner parts.

The writer succeeded in accomplishing the desired results in an experimental way and proved that the principle is sound and that an improved quality of leather results from its use. He built a miniature drying tunnel of galvanized iron 10 ft. long by 5 ft. wide by 5 ft. high. At each end was soldered a truncated pyramid of galvanized iron terminating in a 2-ft. length of galvanized pipe 1 ft. square. An air-tight door was placed in the side of the tunnel to permit workmen to enter to hang up leather and take it out. The terminal pipes were also equipped with air-tight doors, which could be closed at will. Attached to one end was a unit heater and blower. In the pipe at each end was placed a wet-and-dry-bulb hygrometer and an anemometer, which could be read through a window in the pipe.

The inside of the tunnel contained racks for hanging 12 sides of 20 sq. ft. each. It had been demonstrated that the average water content of the stock used in these tests was 64 percent when first hung to dry. This means that 100 lbs. of wet leather contained 36 lbs. of dry leather and 64 lbs. of water. In order to have a water content of 34 percent, 36 lbs. of dry leather would require 18.55 lbs. of water, making a total of 54.55 lbs. of leather of 34 percent water content. In order to bring 100 lbs. of the wet leather to leather of 34 percent water, it is necessary to remove from it 45.45 lbs. of water. Now all that is necessary to reduce the water content of the leather in the tunnel to an average of 34 percent is to drive off 45.45 lbs. of water for each 100 lbs. of wet leather hung in the tunnel.

When everything is ready to start drying a pack of leather, the unit heater and blower is turned on and simultaneously both anemometers are started for recording. At short intervals, the wet-bulb and dry-bulb temperatures are read at both ends of the tunnel and recorded. From each pair of readings, the relative humidity is found from Table 47. From the dry-bulb temperature, the weight of water in 1000 cu. ft. of saturated air is found in Fig. 336. This value is multiplied by 0.01 times the percent relative humidity to get the lbs. of water per 1000 cu. ft. of air at the point where the reading was made. This value is multiplied by the anemometer reading in 1000 cu. ft. for the interval of reading to get the number of lbs. of water passing the instruments in that interval. For each interval, the number of lbs. of water passing the instruments at the inlet end is subtracted from the number of lbs. of water passing the instruments at the outlet end to get the number of lbs, of water that has been driven from the leather. When the number of lbs. of water driven from the leather equals 45.45 lbs. per 100 lbs. of wet leather originally hung in the tunnel, the unit heater and blower is shut off and the air-tight doors at both ends are shut. At this point, the average water content



Courtesy Special Equipment Co.

Fig. 342. Peeling Pasted Skins from Plate After Drying.

of the leather in the tunnel is 34 percent, but it is not evenly distributed. Inside the tunnel there are unit heaters and blowers which are now turned on to set up violent currents of heated air. Since water can no longer enter or leave the tunnel, the portions of leather that were dryer take up water while those that were wetter give up water until all the leather reaches equilibrium with the air confined in the tunnel. The higher the temperature inside the tunnel and the more violent the circulation of the air over the leather, the more quickly is equilibrium established. Finally the leather contains its 34 percent of water uniformly distributed, and is ready for staking and tacking to dry. It requires very few hours to dry leather in this way and it permits an excellent control over the properties of the leather.

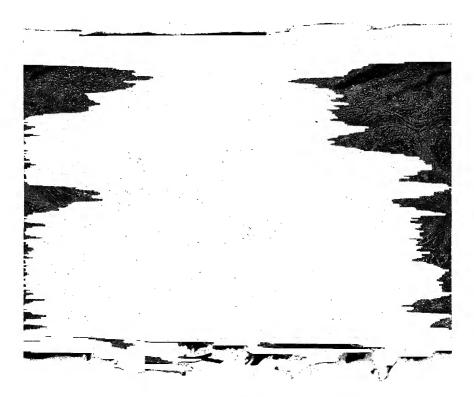


Fig. 343. Vertical Section of Chrome-tanned Calf Leather Hung to Dry, Dampened, Staked and Then Tacked to Dry.

Location: butt.

Thickness of section: 30 microns, or 0.00118 inch.

Magnification: 125 diameters.

In some tanneries, the improper drying of leather and conditioning for staking have caused more damage to leather than all other faults in the tannery combined. An experimental drying unit of this kind is inexpensive, and with it a tanner can obtain so much valuable information regarding his own drying problems that the writer recommends the installation of one to every tanner.



Fig. 344. Vertical Section of Chrome-tanned Calf Leather Pasted to Dry Without Temperature and Humidity Control.

Location: butt.

Thickness of section: 30 microns, or 0.00118 inch.

Magnification: 125 diameters.

Pasting

Some tanners take their chrome-tanned leathers after fatliquoring, coloring and setting out and paste them onto frames of metal, porcelain, plate glass or other materials to dry. They coat the grain surface with a paste made from dextrine or other suitable material and place the leather grain side down onto the smooth surface of the plate or frame. They then proceed to set the leather out by hand so that the grain surface adheres to the plate, and in this condition the leather is dried. One result is a leather of remarkable smoothness of grain surface. The leather adheres to the plate so tenaciously that it allows little or no shrinkage to take place during drying. After drying, the leather can be peeled from the plate as shown in Fig. 342.

One reason for abandoning the old method of tacking wet leather to dry was that the tension caused the fibers to rupture during drying. This made the leather loose and pipey. Essentially the same conditions exist when leather is

pasted. Soon after the advent of the pasting process, the writer made a number of comparative tests and found that pasted leathers were as badly broken up during drying as leathers tacked out to dry from the wet state. Fig. 343 shows a cross-section of finished calf leather that was hung to dry, dampened back and staked, and then tacked to dry. Fig. 344 shows a cross-section of a comparative skin that was pasted from the wet state and dried. The effect of drying under tension is clearly revealed by the numerous ruptured fibers. In this comparison, it seems probable that the ruptures were caused by the cohesions of the fibers during the drying before the forces tending to cause shrinkage became very great. Then,

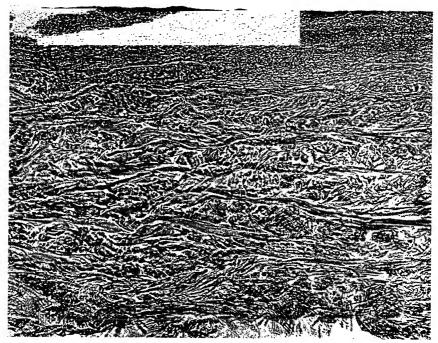


Fig. 345. Vertical Section of Chrome-tanned Calf Leather Pasted to Dry Under Specially Controlled Conditions of Temperature and Humidity.

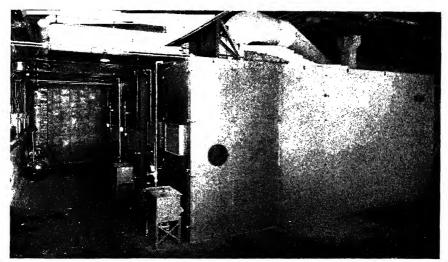
Location: butt.

Thickness of section: 30 microns, or 0.00118 inch.

Magnification: 350 diameters.

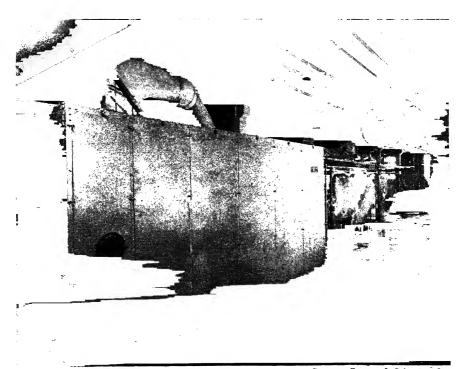
since the fibers could no longer slide over one another, they were ruptured one by one as the forces tending to cause shrinkage increased. No such ruptures take place when leather is tacked out to dry after dampening and staking.

Modern control of temperature, relative humidity and rates of air flow through the drying tunnels has apparently eliminated the looseness of structure that used to be associated with pasted leathers. By drying at higher temperatures with high relative humidities of the air, apparently the forces tending to cause shrinkage can be brought into play before the forces of cohesion glue the fibers together. Since the fibers can still slide over one another, when the great forces of shrinkage



Courtesy Proctor & Schwartz, Inc.

Fig. 346. Front and Side View of 3 Proctor Impinge Aire Pasting Dryer Units.



Courtesy Proctor & Schwartz, Inc.

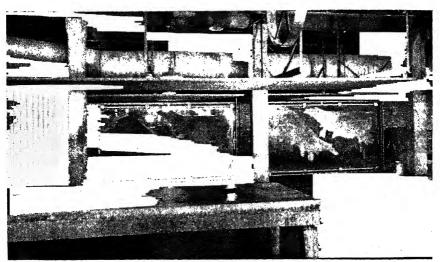
Fig. 347. Same as Fig. 346, but Looking along Side Toward Pasting Frames in Rear.

become active, they are relieved by the fibers sliding out in horizontal directions. Fig. 345 shows a cross-section of finished calf leather that was dried while pasted to a plate under controlled conditions of humidity and temperature. The fibers are not broken up at all. The finished leather was very smooth and tight and a great gain in area was obtained, but at the expense of the thickness of the leather.

The same conditions would, of course, also obtain with wet leather tacked or toggled to dry, but the pasting method has the advantage of making the grain sur-

face very smooth.

In some tanneries, when the leather is taken from the plates, a small amount of water is used to remove the paste from the leather, and the stock is piled over night to sammy, or condition. It is then staked and sent to be finished.



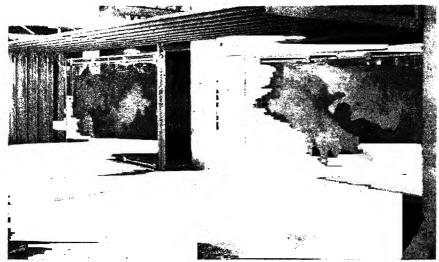
Courtesy Proctor & Schwartz, Inc.

Fig. 348. Same as Fig. 346, but Looking at Pasting Table in Rear and Frames Slid Out of Drying Units to Show Pasted Sides on Glass Plates.

Drying Equipment

Most manufacturers of drying equipment have a special free consulting service for tanners to consider individual problems. Much of the general equipment has already been described, and it will probably suffice here to give a manufacturer's description of an individual installation. The following was furnished by Proctor & Schwartz, Inc. Figs. 346, 347, 348 and 349 illustrate 3 Proctor Impinge Aire Pasting Dryer Units. Each unit contains 9 glass pasting frames, 5'11" by 11'5", used for drying wet cow sides and kip sides. The cow sides have an average wet weight of 7½ lbs. and an average air-dry weight of 3½ lbs., leaving 4 lbs. of water to be evaporated per side. The kip sides have an average wet weight of 4½ lbs. and an average air-dry weight of 2 lbs., leaving 2 lbs. of water to be evaporated per side.

Each 9-frame-unit has a capacity of 18 cow sides, 2 per frame, or 1 on each side of each glass plate, or 36 kip sides, 4 per frame, or 2 on each side of each glass plate. The drying time is 3 hours with a dry-bulb temperature of 120° F. and a wet-bulb temperature of 98° F., using 3-lbs. exhaust steam. The hourly con-



Courtesy Proctor & Schwartz, Inc.

Fig. 349. Same as Fig. 346, but Looking Toward Rear of Drying Units with Two Frames Slid Out to Show Stock on Glass Plates.

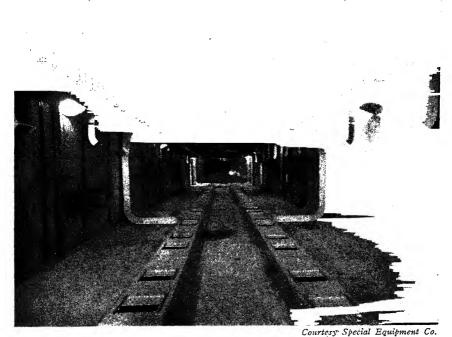


Fig. 350. Interior of Modern Leather-drying Tunnel.

sumption of steam is 123 lbs. and the hourly evaporation of water is 24 lbs. for cow sides and 30 lbs. for kip sides. The capacity of each unit per hour is 6 cow sides or 12 kip sides.

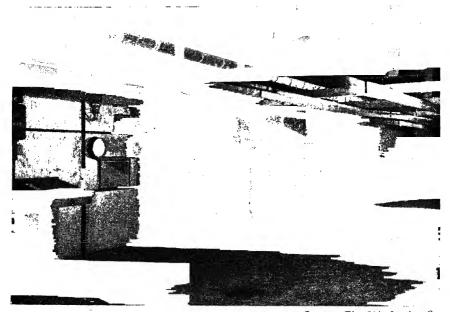
Each unit is provided with a wet-and-dry-bulb, air operated, recording temperature control. The equipment is furnished with air compressor, tank and $\frac{3}{4}$ -H.P. motor and with 2 36"-diameter special fans for circulating air. These fans are mounted on the shaft extensions of 2 5-H.P., 1740-r. p. m. motors. Each unit is provided with 1 18"-diameter special exhaust fan mounted on the shaft extension of at 1-H.P., 1740-r. p. m. motor.

The low temperatures and rapid drying are accomplished by a very unique system of impinge air flues between two adjacent frames. Static pressure of the air is obtained in these flues through the medium of a special type fan. These flues are perforated, thereby admitting air at right angles to the surface of the material being dried. This method of drying gives an even tension to the entire surface of the leather, as all the air striking the material is of the same temperature and moisture content.

This type of drying unit is used also for stock toggled after staking, as shown earlier in the chapter.

Fig. 350 shows another type of drying unit in which the frames are suspended from endless-chain belts, and move from one end of the tunnel to the other. In the distance can be seen a frame with the leather pasted on the plate. The positions of the air ducts in the floor and on the side walls allow vigorous circulatory motion of the air between and around the leather on the frames.

Fig. 351 shows the outside of a drying tunnel in a large calf tannery with the operator observing the temperature and relative humidity on a recording



Courtesy The Ohio Leather Co.

Fig. 351. Outside of Drying Tunnel in Large Chrome-calf Tannery.



Courtesy The Ohio Leather Co.

Fig. 352. Skilled Operators Buffing the Grain Surface of Chrome-tanned Calfskins.

hygrometer. In some systems operating at high temperatures, relative humidities are maintained at optimum values at different points in the tunnel by injecting steam into the air during the drying operation.

Although great advances have been made in our knowledge of the drying of leather, resulting in improved quality of leather and lowered costs of drying, the writer believes that very much greater advances still remain to be made.

Buffing

From the descriptions of hide damage given in Chapter 5 and the frequency of occurrence of grain damage, a layman might well wonder how it is possible to make so much leather with a grain surface of pleasing appearance. A very large amount of leather is greatly improved in appearance by buffing the grain surface before finishing. Buffing consists essentially of sandpapering the grain surface. By referring back to Fig. 8 of Chapter 1 (p. 31) the fibril structure of the grain surface of a tanned calfskin can be seen. In sandpapering the grain surface of leather, the sharp edges of Carborundum, or other abrasive material, cut these microscopic fibrils and produce on the surface a very fine nap. Many grain defects that are displeasing to the eye do not penetrate into the leather nearly to the depth of the grain layer, and such defects can be entirely removed by buffing. If the grain surface is buffed only lightly, the grain pattern is not destroyed, and the finishing operations, in which plastic materials are used to coat the leather, leave the leather so smooth that only an expert can tell the leather has been buffed.

Only when the leather is buffed to a measurable depth, as it must be when the grain damages are great, is the leather referred to as buffed. When the leather is

buffed to a lesser depth, the leather is referred to as *snuffed*. When the leather is buffed so lightly as not to impair the grain pattern, the leather is referred to as having a *corrected grain*.

Fig. 352 shows a battery of buffing machines with operators buffing the grain surfaces of calfskins. In the machine in the foreground, the buffing cylinder can be seen touching the surface of a calfskin. Fitting snugly around this cylinder is a sheet of Carborundum paper with its ends clamped tightly into a horizontal slot in the cylinder. The cylinder revolves at high speed and when a skin is fed into the machine, it is forced against the cylinder while moving forward. The grain is thus buffed over a long path about 8 inches wide. The skin is then shifted and another path is buffed until the entire surface has been buffed; Carborundum papers of many different grain sizes are used to get desired effects. Sometimes a skin is buffed first with a coarse-grained paper to cut to the desired depth and then with a finer paper to produce a finer effect.

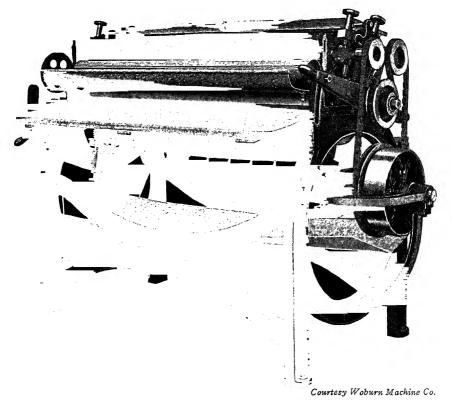


Fig. 353. Seasoning and Blacking Machine.

Buffing requires expert work and good judgment on the part of the operator in order to get exactly the desired result and to prevent marks from showing where different buffing strokes overlap. Usually this is done by a series of overlapping strokes in one direction followed by a series of strokes at right angles to the first ones.

When a tanner has difficulty in determining just how to buff any particular kind of leather, he can usually obtain the services of an expert without charge by contacting one of the manufacturers of abrasive papers.

When leathers are buffed deeply enough to disturb the color of the grain surface, they are usually recolored by hand or by machine before finishing. When done by hand, the buffed leather is placed flat on a table, grain side up, and a solution of the dye is swabbed over it to give it the color desired. Fig. 353 shows a machine used to do this kind of coloring. It contains a reservoir trough of dye solution and a series of feed rolls and brushes for spreading the dye uniformly over the surface of the leather. The skins or sides are fed into the machine from one side and come out the other. This type of machine is commonly used in making black leathers from buffed stock.

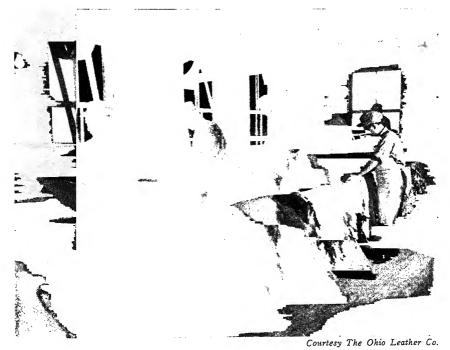


Fig. 354. Buffing Suède Calfskins on Over-shot Buffing Machines.

Buck Leathers

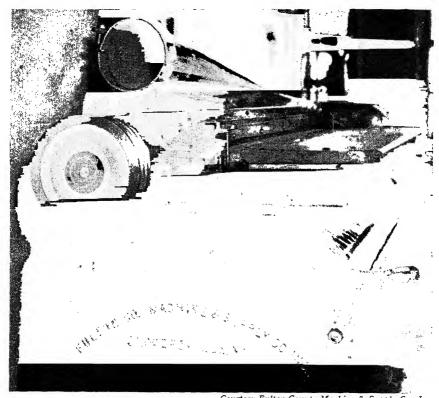
Buck leathers are made from cow sides by buffing the grain surface, coloring to the desired shade and then incorporating into the buffed surface very finely divided powders of inert pigments of the desired color. This still leaves a nap on the surface and a soft velvety feel.

Suede Leathers

Suède leathers are made from very small skins, some of the best being made from the skins of unborn calves, called *slunks*. The reason very small skins are best is that they are finished on the flesh side with a velvety nap; the smaller

the fibers, the finer the nap that can be produced. The skins of unborn or prematurely born animals have the advantage of very fine fibers and also of much less highly developed blood vessels. The buffing is done on the flesh side and the leather is not colored until after buffing.

The stock is dried after fatliquoring without coloring. It is then dampened back to a water content of about 34 percent and staked. While still damp, it is buffed on the flesh side on an emery wheel, which is better than Carborundum paper for wet leathers. One of these emery wheels can be seen in the foreground at the



Courtesy Fulton County Machine & Supply Co., Inc. Fig. 355. Fulton County Buffing Machine.

extreme left of Fig. 354. It is set into a table with only a part of it sticking through the table top and presenting the appearance of an automobile tire. This type of buffer is generally known as an *over-shot buffer*. Fig. 354 shows a battery of operators buffing the flesh sides of calfskins in the making of suède leathers. With the emery wheel running at high speed, the operator draws the skin over it, adjusting pressure and location to produce a fine, uniform nap all over the flesh side. Some tanners buff the stock on a regular buffing machine with Carborundum paper, in which case they tack the leather to dry after staking and then buff the leather only when dry. The leather is then wet back thoroughly, washed, dyed and dried again. It is then dampened again, staked and buffed again lightly, which is

referred to as top buffing. It is then milled in a dry drum to soften it and is tacked or toggled to dry. Sometimes the fatliquoring is done together with the dyeing after buffing. Great care must be exercised to avoid greasiness of the napped surface, and this is why some tanners of white suède leathers use only 1 percent on shaved weight of Gardinol (du Pont) in place of fatliquor.

Wetting Agents

After chrome-tanned leathers have been dried, they wet back with difficulty, and so some tanners make use of wetting agents. Many of these agents are available commercially, of which we might mention the Duponols and Neomerpins of the du Pont Co. as typical. Duponol is the registered trademark designating certain higher aliphatic alcohol sulfates and their derivatives offered by the du Pont Co. Some of the Duponols and Gardinols are identical. Neomerpin-N is a free naphthalene sulfonic acid that is used where wetting under acid conditions is desired.

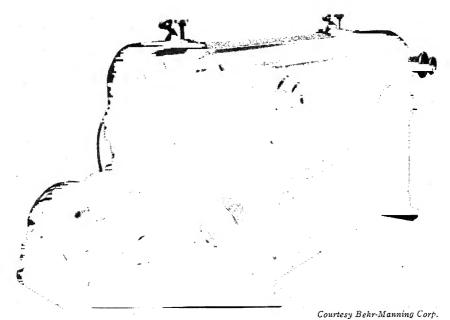
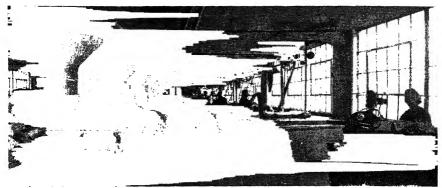


Fig. 356. Lightning Buffing and Shaving Machine.

Difficulties encountered in wetting back chrome-tanned leathers can frequently be eliminated by drumming the stock with a 4-percent solution of Duponol-WA. A remarkable series of wetting, emulsifying and dispersing agents has recently been introduced by Röhm & Haas Co. under the name of Triton that will interest most tanners. Progress is continually being made in the development and uses of wetting agents and the various manufacturers are glad to give the tanner all results that are available.

Other Types of Buffing Machines

When only small skins are to be buffed, special buffing machines are available that present a great saving in labor and require less skill in operation. These



Courtesy L. H. Hamel Leather Co.

Fig. 357. Finishing Department of Goatskin and Sheepskin Tannery.

machines use a greater width of Carborundum paper. One type of machine that has been used satisfactorily on both suède and buck leathers is shown in Fig. 355.

Another type of buffing machine much liked by many tanners is the combination Lightning Buffing and Shaving Machine shown in Fig. 356, made by Curtin-Hebert Co., of Gloversville, and distributed by the Behr-Manning Corp., of Troy, New York.



Courtesy L. H. Hamel Leather Co.

Fig. 358. Staking and Trimming Department of Goatskin and Sheepskin Tannery.

Practically all types of buffing machines for buffing dry leather are equipped with suction devices for removing the fine leather dust resulting from the buffing action. The larger machines for whole skins usually also have cylindrical brushes for brushing the leather dust from the skins.

Brushing

With the older type of buffing machine, the leather after buffing is usually heavily coated with leather dust which is brushed off either by hand or with a special brushing machine with cylindrical brushes housed in an air-tight table. leather is introduced between the revolving brushes through a slot in the table and is thus cleaned preparatory to finishing. In Fig. 357 an operator can be seen feeding a skin into a brushing machine that has just been buffed on a buffing machine beyond him. This is a scene in the finishing department of a large goatskin and sheepskin tannery. The girl in the right foreground is measuring the thickness of skins on a special machine and assorting the stock according to grades. The piles of leather at the left consist of unfinished leather, usually referred to as leather in the crust. Fig. 358 shows another department in the same tannery where goatskins are being staked. In the left background, leather is being trimmed to free it from loose ends and ragged edges and make it more presentable.

References

- Lindsay, D. C., Drying and processing of materials by means of conditioned air. Carrier Engineering Corp., Newark, N. I., 1929.
 Heating, ventilating, air-conditioning guide. Vol. 18. American Society of Heating and Ventilating Engineers, New York, 1940.

Chapter 17

Finishing Light Leathers

The finishing of light leathers has for its objects making the leather more pleasing to the eye and more serviceable in use. Most methods of finishing involve coating the exposed surface with plastic materials and then treating the leather mechanically in various ways. The plastic materials and combinations of them used in finishing leathers are usually referred to as finishes. Back in the days when tanning was done on farms, common leather finishes were milk, ox blood, and the whites of eggs. By coating the grain surface of leather with milk or with egg white, allowing it to dry and then rubbing it, a pleasing luster was obtained. As tanneries grew in size, complexity and specialization, many other finishing materials were put to use. To casein and albumens were added shellac, waxes and many other materials. Later it was found that inert mineral pigments, such as iron oxide, could be ground in aqueous solutions of the various finishes and would serve to hide minor defects in the surface of the leather. With the great development of modern plastics, many new types of finishing materials were made available for leather, with somewhat astonishing results. Today there are many factories devoted entirely to the manufacture of leather finishes of secret composition, many of which produce such valuable effects on the leather that a tanner can well afford to pav the premium required to get these finishes prepared for use rather than to rely upon the much cheaper finishes that he can readily prepare himself.

In the modern tannery, all the simpler types of finishing materials are prepared at the tannery, and the more complex finishing materials, that change with the styles and demands for special types of leather, are purchased from finish manufacturers, who perform a great service to the tanner by keeping abreast of the styles and of changing demands. Since the finish manufacturer is really in competition with the tanner himself, he must keep secret the composition of new finishes that he develops, at least until his profits are sufficient to pay for the cost of the development. For this reason, we shall have to refer to some finishes described later in this chapter only by their trade names.

The great majority of finishing materials used on leather are prepared by the tanners themselves. These will be described first in connection with the finishing of the types of leather on which they are used. In describing the preparation of each finish, a number or letter or both will be given to each to identify it in subsequent references to its use.

Simple Finishes for Chrome-tanned Calf Leathers

Finish No. 1 (ammonia-casein): Weigh 100 lbs. of casein into a suitable tank or barrel near a live-steam line. Cover the casein with 40 gals. of water at 70° F. and let it soak for 1 hour. Then add 11½ lbs. of 26° Baumé aqua ammonia (29.4 percent ammonia) with stirring, and allow to stand 1 hour. Then bubble live steam into the mixture until the boiling point is reached. Then put a loose-fitting cover onto the tank or barrel and let live steam bubble gently into the mixture for 8 hours, which will increase the volume to about 90 gals. Continue to stir while adding 3 lbs. of Collatone (Lehn & Fink) dissolved in 4 gals. of water, as a preservative, followed

by 4 lbs. of formalin (40 percent formaldehyde), which acts as a hardening agent for the casein. After cooling, dilute with water to 100 gals. and strain through cheese-cloth.

Finish No. 1a (ammonia-casein): Proceed exactly as for Finish No. 1, but use only 5 lbs. of aqua ammonia and do not continue to boil after raising the temperature to the boiling point.

Finish No. 2 (ammonia-shellac): Weigh 100 lbs. of bleached shellac into a suitable tank or barrel near a live-steam line. Add 17 lbs. of 26° Baumé aqua ammonia in 20 gals. of water and boil mixture with live steam until all the shellac has dissolved. Then dilute with water to make a total of 50 gals. and strain off any wax present through cheese-cloth.



Fig. 359. Stock Room for Crome-tanned Calfskins Awaiting Selection for Finishing.

Finish No. 2a (borax-shellac): Dissolve 33½ lbs. of borax in 40 gals. of boiling water and add 100 lbs. of bleached shellac. Continue to boil until all the shellac is dissolved. Dilute to 50 gals, with water and strain through cheese cloth.

Finish No. 3 (carnauba wax): Dissolve 6 lbs. of castile soap in 25 gals. of boiling water. Melt 30 lbs. of carnauba wax at a temperature of 190° F. and pour it, while stirring vigorously, into the boiling soap solution. Continue to boil the mixture for 5 minutes, cool and dilute with water to make 50 gals. Add 2½ lbs. of oil of mirbane as a preservative and mix well.

Finish No. 3x (colored carnauba wax): This is made exactly like Finish No. 3 except for dissolving 12 oz. of wax-soluble dye in the 30 lbs. of molten carnauba wax before pouring it into the boiling soap solution. Use the name or color of the dye in place of the letter x in designating the finish.

Finish No. 4x (pigment finish): A great variety of colored pigments may be used to make this finish, but only one of a popular color will be given to illustrate the principle of making it. These pigments are purchased in the form of finely ground powders. Mix 140 lbs. of medium chrome yellow, 57 lbs. of Indian red, 85 lbs. of burnt sienna and 30 lbs. of burnt umber with 120 lbs. of sulfonated castor oil and grind in a pigment-grinding mill until a smooth and uniform paste is obtained. The mixture may be put through the mill several times, if necessary.



Fig. 360. Finishing Chrome-tanned Calfskins by Hand Swabbing.

Designate each different mixture of pigments by a color number or letter to be used in place of the letter x in designating the pigment finish. Different pigments require different proportions of sulfonated oil in grinding as indicated in Table 48.

Finish No. 5 (black chrome-calf finish): Mix 24 fl. oz. of Finish No. 1, 24 fl. oz. of Finish No. 3x (in which x represents the oil-soluble Nigrosine-B), 20 fl. oz. of a 5 percent solution of Nigrosine-J, 20 fl. oz. of a 5 percent solution of Nigrosine-B and 50 fl. oz. of a 5 percent solution of logwood crystals. Mix separately 20 fl. oz. of a 5 percent solution of Nigrosine-RB, 12 fl. oz. of ox blood, 3.8 fl. oz. of diethylene glycol (Carbide & Carbon Chemicals Corp.) and 0.2 fl. oz. of sulfonated linseed oil. Mix these two solutions and add 258 fl. oz. of water. Mix well, strain through cheese-cloth and the finish is ready for use. The diethylene glycol and sulfonated linseed oil act as plasticizers to prevent the finish on the leather from becoming too hard and dry.

Finish No. 6 (bottom finish for colored chrome calf): To make 1 gallon: To

5 oz. of Finish No. 4x, add 13 fl. oz. of Finish No. 1 and mix well. Then add $1\frac{1}{4}$ oz. Finish No. 3x (in which x represents wax-soluble yellow), $\frac{1}{2}$ oz. Finish No. 3x (in which x represents wax-soluble red) and 0.05 oz. Finish No. 3x (in which x represents Nigrosine-B). Then add 20 fl. oz. of Finish No. 1a, 19 fl. oz. of a 1 percent solution of phosphine, 5 fl. oz. of a 1 percent solution of safranine and 3 fl. oz. of a 1 percent solution of Nigeria black. Then add $\frac{1}{2}$ fl. oz. of formalin (40 percent formaldehyde). Dilute with water to make 1 gal., mix well and strain through cheese-cloth for use.

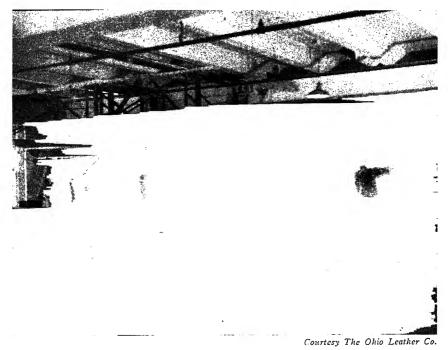


Fig. 361. Tunnels for Drying Chrome-tanned Calf Leathers after Finishing.

Finish No. 7 (second finish for colored chrome calf): To make 1 gallon: Mix 11 fl. oz. of Finish No. 1a, 9 fl. oz. of a 1 percent solution of phosphine, $4\frac{1}{2}$ fl. oz. of a 1 percent solution of safranine and $6\frac{1}{2}$ fl. oz. of a 1 percent solution of Nigeria black. Dilute with water to make 1 gal. and mix well.

Finish No. 8 (top finish for colored chrome calf): To make 1 gallon: Mix 4 fl. oz. of Finish No. 1, 5 fl. oz. of Finish No. 2, 2 fl. oz. of Finish No. 2a with water to make 1 gal.

Finishing Black Chrome-tanned Calf Leather

This procedure is for full-grain calf leather taken after restaking after final drying, as described in Chapter 16. Fig. 359 shows a stock room where dried and staked chrome-tanned calfskins are stored awaiting selection for various types of finishing. Each skin is laid out flat on a marble-top table, grain side up, as shown in Fig. 360, which will be used to illustrate the method of applying this finish.

Fill a large pan with Finish No. 5. Wet a sponge with the finish and coat the grain surface of the leather by a series of strokes across the skin and back from belly to belly, overlapping with each stroke, and continuing the succession of strokes from head to tail. Following each series of strokes, a second operator on other side of the table wipes off any surplus finish with a plush swab, using the same kind of strokes as those used in applying the finish. The second operator really smooths out the finish to avoid any streaks showing. After this coat of finish has been applied, the skin is dried quickly, but thoroughly, often by passing through a drying tunnel. The entrance to one of these tunnels can be seen at the right of Fig. 360 with skins hanging from hooks set in cross bars. Fig. 361 shows the openings of such drying tunnels. When the leather is thoroughly dry, it is ready for glazing.

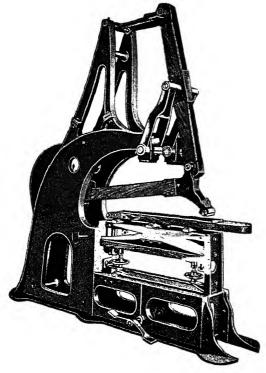


Fig. 362.

Horizontal-bed Glazing Jack.

Courtesy Woburn Machine Co.

Glazing

A horizontal-bed glazing machine is shown in Fig. 362 and a battery of glazing machines in use in a calf tannery is shown in Fig. 363. The glazing machine for this type of work usually has a bed sloping downward from the operator. On this bed, there is a strip of heavy leather covering the path of movement of the glazing jack, which consists of a solid cylinder of glass attached to the end of a moving arm. The glass cylinder is so clamped to this arm that it cannot revolve. When the machine is running and a skin is laid on the leather strip on the bed of the machine, the arm comes forward with the glass cylinder raised. It then forces

the cylinder down onto the leather with considerable pressure and pulls backward while pressing tightly against the leather, producing great friction along the path of the grain surface of the skin backed by the heavy strip of leather below. With each stroke of the glazing jack, the operator shifts the position of the skin so that it is finally glazed over its entire area. The heat generated by the friction of each stroke is so great that it softens the carnauba wax in the finish of the leather so as to produce a continuous plastic mass of great luster in the grain surface.



Courtesy B. D. Eisendrath Tanning Co.

Fig. 363. Glazing Finished Chrome-tanned Calfskins.

In glazing skins for the first time, it is very important that it be done with as heavy a pressure as is practical. The first glazing operation also brings about cohesions of the fibers in the grain surface which it is necessary to break up before proceeding with the second application of finish. After glazing, each skin is drystaked lightly to break up these cohesions. The skins are then smooth-plated.

Plating

After glazing and staking, the skins are smooth-plated in a specially designed press, like that shown in Fig. 364. Each skin is laid, grain side up, onto the bed of this press and then the bed is raised against a smooth steel plate heated to 150° F. with a pressure of about 300 tons. This tends to make and keep the leather very smooth and dense. Both temperature and pressure of the smooth plate can be regulated according to needs. Often the leather being plated is of greater area than the bed of the press, in which case only a portion of it is fed into the press

at a time. The press shown in Fig. 364 is equipped with an interesting automatic safety device. The operator stands on a movable carriage which slides up to the press whenever it is open and moves away from the press as it closes so that he cannot get his hand caught in it while closing.

After smooth-plating, the skins are taken back to be finished a second time with Finish No. 5. Since they have already been finished and glazed, they do not absorb very much of the finish and so dry very quickly. They are not again put through the drying tunnel, but merely hung over racks or horses, one at a time until dry. Fig. 365 shows a group of operators refinishing calfskins and hanging them over special horses to hold only one skin each.

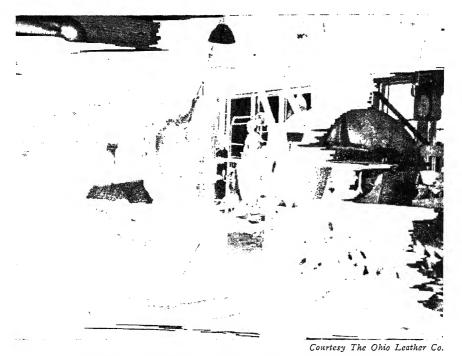


Fig. 364. Smooth-plating Finished Chrome-tanned Calfskins.

When dry, each skin is given a third coat of finish and then thoroughly dried in the tunnel. Each skin is again glazed, using a lighter pressure than on the first glazing, restaked and again smooth-plated, but a lower temperature than before. The stock is then completely finished and awaits only the final assortment and measuring.

Finishing Colored, Chrome-tanned Calf Leather

The finishing of colored leather differs from that of black leather primarily in the use of appropriately colored finishes. This leather has already been dyed a shade which produces, in conjunction with the finishes and finishing operations employed, the color and shade desired on the finished leather. Leather is made in so many different colors and shades that it would be quite impractical to list methods of

making all of them. In fact, many tanners must work with the creators of styles and change their colors from time to time. A method will be described for finishing one popular shade of tan in order to illustrate the principles involved, from which the tanner can work out various colors, according to his needs. It should be pointed out that the glazing operation deepens the color considerably while producing the mirror luster.

Each skin is coated on the grain side with 4 very light coats of Finish No. 6, drying after each coat. In Fig. 366 operators can be seen finishing chrome-tanned calfskins. Each operator has a drying rack with 12 radial arms. As soon as he has finished a skin, he hangs it over one of these arms. After he has coated 12



Courtesy I he Unio Leatner

Fig. 365. Refinishing Chrome-tanned Calfskins.

skins, the first one is dry enough to receive the second coat. He continues in this way until each of the 12 skins has received 4 coats each, when they are sent to be thoroughly dried in the tunnel. The operator then starts finishing a second set of 12 skins. Some tanners apply all of this first finish as a single coat, but the results obtained by applying it in a succession of much thinner coats are much more uniform and finer.

After the skins are thoroughly dry, they are glazed with the highest pressure that is practical. Fig. 367 shows another interesting view of a battery of glazers at work on chrome-tanned calfskins. After glazing, the skins are dry-staked and smooth-plated at high temperature and pressure.

After smooth-plating, the skins are returned for the second finishing, which consists in applying a single coat of Finish No. 7, after which the skins are glazed a

second time under high pressure, dry-staked and returned for the third finishing, which is given by applying a single coat of Finish No. 8. The skins are dried again and then glazed under low pressure. They are again dry-staked and smooth-plated at lower temperature and pressure than before. They are then trimmed to present a neat outer edge, as shown in Fig. 368, and are sent on for final measuring and grading.

In finishing colored chrome-calf leathers, it will be noted that the pigment finish was used only in the bottom coat and shellac only in the top coat. The pigment is used to hide minor defects in the grain surface and it tends to dull the



Courtesy The Ohio Leather Co.

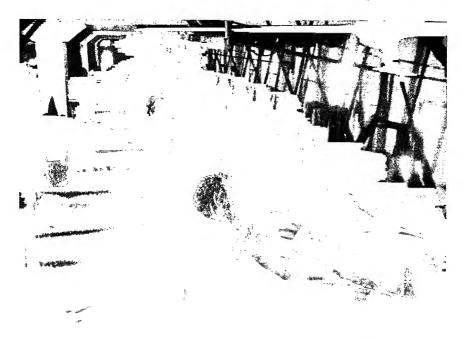
Fig. 366. Finishing Chrome-tanned Calfskins with a Succession of Very Thin Coats.

luster of the finish. Shellac, on the other hand, develops a high luster. Egg albumen and blood albumen also develop high lusters and are often used as top finishes. Usually materials of this kind that produce high lusters make the finish very hard and, if used in too great quantity, the effect of this is what is known as a crusty break.

The Break of Leather

If the grain surface of a piece of leather is bent so that it is sharply concave, it will be noted that it breaks up into tiny wrinkles. If these wrinkles are very fine and there are many of them to the linear inch, the leather is said to have a *fine break*. If the wrinkles are large and there are fewer of them per linear inch, the leather is said to have a *coarse break*. To the average person, a fine break on leather is more pleasing to the eye than a coarse break; tanners of upper leathers therefore strive

to produce the finest break possible in their leathers. In order to get a fine break, it is necessary to prevent great cohesion of the fibrils of the grain surface, which is one reason that the leather is dry-staked after glazing. When too much shellac or albumen is used in a finish, it may become very hard and the break may be coarse. An even more serious defect is that the break, once having been formed by flexing the leather, remains even after the leather has again been allowed to lie flat. Handling leather with this defect, and any undue flexing of it, produces an unsightly appearance of the grain surface that is known as a crusty break, or a finish break. Some manufacturers of leather finishes have developed shellac mix-



Courtesy The Ohio Leather Co.

Fig. 367. Showing a Battery of Glazing Machines Operating on Chrome-tanned Calfskins.

tures that are so soft and flexible that they do not produce a crusty break even when used in large quantity.

Aniline Leathers and Pigment Leathers

When leathers are buffed very deeply in order to hide grain defects, it is often necessary to use large amounts of pigment in the finish to get uniform appearance. The more pigment used, the more binding material, such as casein, must be used to prevent the pigment from chalking and flaking off. A heavily buffed leather completely covered by pigment is definitely classed as a pigment leather. Some skins have grain surfaces so nearly perfect that no pigment at all is needed to produce a uniform appearance. Such leathers finished entirely without the use of pigments are known as aniline leathers. Sometimes the uniformity of appearance of a piece of leather is greatly improved by amounts of pigment so small

that they do not hide the true grain surface. When improved in this way by the use of small amounts of pigment, the leather is still classed as an aniline leather and not as a pigment leather.

Simple Finishes for Vegetable-tanned Calf Leathers

Vegetable-tanned leathers differ so much in their properties from chrometanned leathers as to require different types of finishing materials in order to get the best results. These finishes will be designated by numbers continuous with those described for chrome-tanned leathers.

Finish No. 9 (flaxseed-gelatin-albumin): Soak 3½ lbs. of flaxseed in 4 gals. of water at 70° F. over night. Next morning boil the mixture for 10 minutes. Add



Courtesy The Ohio Leather Co.

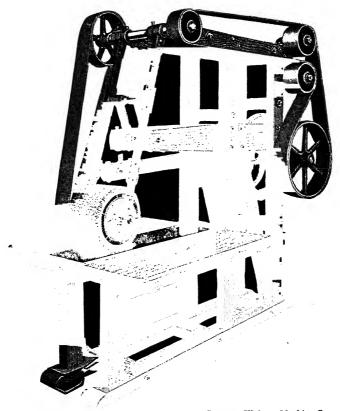
Fig. 368. Trimming Finished Chome-tanned Calfskins.

3½ oz. of Collatone in 10 gals. of water at 70° F. as a preservative, and strain through a copper sieve. Soak 26 oz. of gelatin in 8 gals. of water at 70° F. over night. Next morning heat until the gelatin is completely dissolved and add to the flaxseed decoction. Soak 2.8 lbs. of dried egg elbumin in 8 gals. of water at 70° F. over night, or until entirely dissolved, and add to the above mixture. Dissolve 1½ lbs. of castile soap in 3 gals. of boiling water and then add 15 gals. of water at 70° F. and add to the above mixture. Mix well and the finish is ready for use.

Finish No. 10 (pigment finish): Add 8 oz. of Finish No. 4x of desired color to each gallon of Finish No. 9. Mix well and it is ready for use.

Finish No. 11 (casein-shellac): Mix 20 gals. of Finish No. 1 with 2 gals. of Finish No. 2. Dilute with water to make 50 gals. and add 4 fl. oz. of Oil of Eucalyptus as a preservative.

Finish No. 12 (carnauba wax): Weigh 2½ lbs. of castor oil into a brass container and add, while stirring, 5 oz. of caustic soda dissolved in 9 fl. oz. of water. Heat, while stirring, until the mixture becomes a uniform liquid. Heat 27 lbs. of carnauba wax to 190° F. and maintain this temperature, while stirring, until the wax is completely liquid. Stop heating and add the oil mixture to the molten wax slowly, while stirring. Continue to stir until the mixture no longer gives off steam. Then pour the molten mixture into 15 gals. of boiling water, while stirring vigorously. Continue stirring while cooling the mixture as rapidly as possible. Filter through cheese-cloth and dilute with water to 50 gals.



Courtesy Woburn Machine Co.

Fig. 369. Leather Brushing Machine.

Finish No. 13 (colored finish): To make 1 gallon: Mix 40 fl. oz. of Finish No. 11 with 40 fl. oz. of Finish No. 12 and add 1 fl. oz. of formalin (40 percent formaldehyde) and 8 oz. of Finish No. 4x of desired color. Add water to make 1 gal. and mix well.

Finish No. 14 (black finish): Work 5 lbs. of Nigrosine-JB into a paste with very little boiling water and continue to add boiling water until complete solution is obtained. Dilute to 10 gals. with cold water and filter. Add 4 gals. of Finish

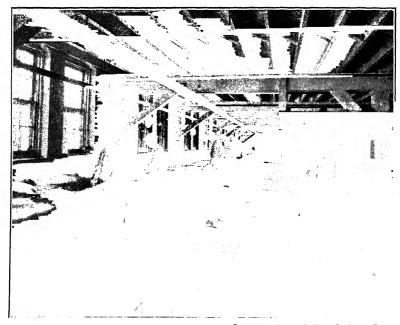
No. 1, 14 gals. of Finish No. 2, 1 gal. of Finish No. 9 and 1 gal. of water containing $1\frac{1}{2}$ oz. of castile soap, 25 fl. oz. glycerin and 8 fl. oz. of Oil of Mirbane as a preservative. Mix well.

Finish No. 15 (vulcanized neatsfoot oil): This belongs to the type of water-proofing materials known in the trade as viscol. The manufacture should be done in a well-ventilated hood, because sulfur monochloride must be used and this is a fuming liquid that is very irritating to the nose and throat. Mix 50 lbs. of 20° cold-test neatsfoot oil with 50 lbs. of naphtha of 0.74 specific gravity. From a glass separatory funnel, add very slowly, while stirring, 8 lbs. of sulfur monochloride (Dow Chemical Co.). As much heat is developed during the addition of the sulfur monochloride, it must be added slowly enough so that the temperature is never allowed to rise above 200° F. After it has all been added, mix well and let stand for a week or more before using.

Finishing Black Vegetable-tanned Calf Leather

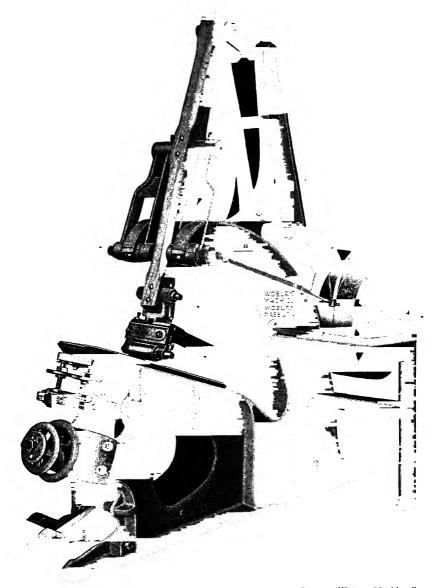
The stock is taken after drying, as described in Chapter 16, and assorted for type of finishing and for colors or blacks. Vegetable-tanned leathers vigorously retain any crease marks or dents, but they can readily be rewet and reset before drying again. It is very important to inspect every skin very carefully for any defects that would require dampening and resetting. Any defective skins are reworked.

Dried skins that have passed inspection are first brushed. Fig. 369 shows one type of brushing machine. A skin is placed on the bed of the machine and the revolving brush comes forward and then descends on the skin and brushes the grain with a backward stroke. With each stroke of the brush, the position of the



Courtesy A. F. Gallun & Sons Corp.

Fig. 370. Trimming Vegetable-tanned Calfskins before Finishing.



Courtesy Woburn Machine Co.

Fig. 371. Rolling Jack for Rolling Vegetable-tanned Calfskins.

skin is shifted by the operator until the entire surface has been brushed. It is customary to rotate the skin during the brushing so that each area has been covered by the brush twice. This is referred to as *brushing twice around*.

After brushing, each skin is dry-staked. Unlike chrome-tanned calfskins, vegetable-tanned calfskins do not have to be staked during the drying operations nor do

they have to be dampened for staking after the first complete drying. After staking, the skins are *trimmed* to remove any rough or straggly edges. Sometimes the entire outer edge to a depth of $\frac{1}{4}$ inch is cut away to give it a neat appearance. Fig. 370 shows a battery of operators trimming vegetable-tanned calfskins before finishing.

After trimming, clean the grain surface of each skin by wiping it with a solution of $\frac{3}{4}$ fl. oz. of aqua ammonia in 1 gal. of warm water. While still damp, brush each skin once around and then smooth-plate under 150 tons pressure at 70° F. Then retack on frames and dry again. Then dry-stake and apply the first coat of finish. This consists of Finish No. 14. One operator applies the finish with a plush swab with a series of overlapping strokes, while an operator on the other side of the table works over the applied finish with another swab to smooth it out. After finishing, each skin is hung to dry at 90° F. for 20 minutes; it is then brushed twice around and rolled.

Fig. 371 shows a Woburn rolling jack, which is very much like the glazing jack, except for the fact that a revolving steel roll replaces the fixed solid glass roll. While the steel roll strikes the grain surface of the skin and rolls over it with considerable pressure, there is no great friction, as in glazing, and no measurable heat is developed. During rolling, the skin is usually rotated so that the entire area is covered twice, which is referred to as rolling twice around.

After rolling, the skins are finished a second time exactly like the first, but after the second finishing each skin is hung to dry in the drying tunnel at 90° F. for an hour, and is then brushed twice around and rolled twice around. If any skin is then not soft and pliable enough, it is dry-staked. Sometimes skins have hard areas, although the rest of the skin may be soft enough, in which case, only the hard areas are staked. If the skins do not appear to be sufficiently well covered with finish, they may be finished a third time in the same manner as the second. After any finishing, the skins are always brushed twice around and rolled twice around.

If the leather is for summer shoes and is not to be waterproofed, it is then smooth-plated at 110° F. under 150 tons' pressure, and is ready for final grading and measuring. If the leather is to be made more water-repellant, it is treated with Finish No. 15. In a room with good ventilation, the grain surface of each skin is swabbed with a solution made by mixing 1 gal. of Finish No. 15 with 9 gals. of naphtha of 0.74 specific gravity. This is applied to the otherwise completely finished leather. Where greater degrees of waterproofness are desired, this finish may also be applied to the flesh side of the leather in amounts desired. Where the leather is made to simulate the original Russian calf tanned with birch bark, the flesh side is coated with a mixture of 1 gal. of Finish No. 15, 9 gals. of naphtha and 2 fl. oz. of birch oil. For wallet leathers, sometimes Oriental perfumes, such as sandalwood oil, civet, musk, etc., are mixed with the birch oil. After this treatment, the leather is hung to dry for 2 days in a drying room where special precautions are taken against the fire hazard of evaporating naphtha.

Finishing Colored Vegetable-tanned Calf Leathers

Dried skins that have passed inspection for colors are first brushed twice around, dry-staked and trimmed. They are then coated on the grain side with Finish No. 10 of the desired color, using two operators, one to apply the finish and one to swab it out smoothly. After applying this finish, hang to dry for 5 min. and then brush twice around and roll twice around. Then hang in the drying tunnel for 1 hour at 90° F. After two or three skins have been finished in this way, inspect them closely for correctness of color. If the color is not exactly as desired, correct it by

adding solutions of appropriate dyestuffs to the finish, and then proceed to finish all of the skins.

The second finish can be applied by hand, but it is more conveniently done with a spray gun. Spray-finishing equipment has now become well established in the finishing of leather. This type of finishing is usually done in booths equipped with wire racks for holding the skins, baffle boards and powerful suction ventilation. Fig. 372 shows a battery of spray booths where calfskins are finished, using spray equipment. Liquid finishes and compressed air are led to a spray gun through appropriate flexible hoses. The gun can be adjusted to deliver a variety of types of spray. Each skin is placed on the wire rack and the operator sprays Finish No. 13 over it in a series of overlapping strokes. Having covered the skin with finish, he



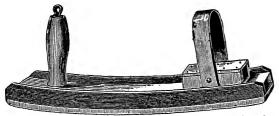
Courtesy The Ohio Leather Co.

Fig. 372. Spray Equipment Used for Finishing Calfskins.

proceeds to coat it a second time with another series of overlapping strokes at right angles to the first strokes. After being sprayed, each skin is hung to dry for 5 min., and is then brushed twice around, rolled twice around and hung in the drying tunnel for 1 hour at 90° F. After all the finishing materials has been applied to the leather, proceed exactly as for black leather, using more or less of Finish No. 15 according to the degree of waterproofness desired in the leather.

Boarding or Graining

The descriptions of finishing so far have been limited to smooth, full-grain calfskins, both chrome-tanned and vegetable-tanned, and the methods given are applicable to any smooth, full-grain leathers. Pleasing patterns can be produced on the

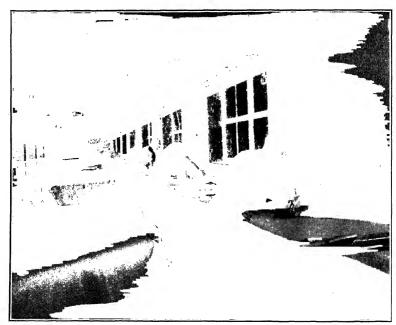


Courtesy Chas. H. Stehling Co.

Fig. 373.

Cork Arm Graining Board.

grain surfaces of calfskins and other finished leathers by an operation known as boarding, or hand graining. This method of producing grain patterns was known long before embossing presses came into use in the tanning industry, but the effects produced by hand graining are still very popular. In hand graining, an operator uses what is known as a graining board, like the one shown in Fig. 373. It consists of a curved board with its face covered by a thick sheet of cork. The operator puts his arm through the loop at one end and takes a firm hold on the grip at the other end with his hand. A skin is laid on the table, grain side up. The operator folds a portion of the leather over so that it rests grain upon grain. He then presses with the graining board upon the fold, forming a crease. He then pulls the board back towards him, while pressing on the fold in the leather. As he does so, the crease line moves along the leather, following the board and producing a series of creases about $\frac{1}{25}$ inch apart. The greater the pressure he applies, the sharper will be the creases and the closer they will be together; that is, there will be more



Courtesy A. F. Gallun & Sons Corp.

Fig. 374. Boarding, or Hand Graining, Vegetable-tanned Calfskins.

crease lines per linear inch. By boarding the skin completely in one direction and then in a direction at right angles to the first, he produces a box-grain pattern. By boarding a third time in a direction diagonal to the other two, he produces a pebbled-grain pattern.

Fig. 374 shows a battery of hand-grainers at work boarding vegetable-tanned calfskins and Fig. 375 shows another group at work on chrome-tanned calfskins.

Ironing

After boarding the leather, the grain surface is again made smooth by ironing it with a hot iron, much as a housewife irons clothes. Although the grain surface is again made smooth, the pattern produced by boarding remains, and the boarded leather is softer and more flexible than it was before boarding. In some tanneries, this ironing is still done by hand with an electric iron, but some tanners have



Fig. 375. Boarding, or Hand Graining, Chrome-tanned Calfskins.

installed large ironing machines, like those to be found in commercial laundries. The fine effect produced by ironing appears not to be obtained by smooth-plating, and some tanners definitely prefer hand ironing to machine ironing because of the easily varied effects of friction and pressure even though the labor cost is much greater.

Embossing

All through the ages, attempts have been made to decorate and beautify leathers, and many valuable works of art are to be found *tooled* on vegetable-tanned leathers.

By working on the grain surface of leather with a hot iron pencil or tool, artists have been able to produce even portraits in relief on leathers. At the plant of Bona Allen, Inc., in Buford, Georgia, one can still find highly skilled artists at work daily tooling beautiful designs in relief on leather saddles and trimmings. This hand work not only requires great skill, but it is enormously time-consuming and expensive. With the development of modern machinery, it was found possible to produce very elaborate designs in relief upon leather by a process of embossing, which has made possible the production of elaborately designed leathers at no greater cost than that of smooth leather. Some embossing designs are very effective in hiding grain damages, and it has been found possible to buff grain-damaged leather and then to finish and emboss it, producing a beautiful piece of leather from an otherwise unsightly skin.

One of the pioneers in the building of embossing presses in this country is the T. W. & C. B. Sheridan Co. of New York and Boston. The writer is indebted to Mr. P. D. Bishop of this company for the following descriptions of the development of the Sheridan press and the latest methods for the building of matrixes for

embossing and for smooth-plating.

"As in a great many cases of machine development, Sheridan presses evolved from small beginnings. The first presses were small units operated by hand, with an embossing surface of 7"×5" or 14"×11". These came along about the middle of the nineteenth century and were used mostly by bookbinders for stamping designs on book covers, either of leather or cloth. The pocketbook and bag manufacturers then took it up, asking for a larger and heavier press to stamp designs on the cut-out pieces of leather.

"The demand for still larger plate surfaces came with the development of leather-covered trunks and the Sheridan press was made of a size to take the whole side of a trunk, with a plate surface $24'' \times 42''$. This type and size of press was also tried as a smoothplating machine on side leather, but the 24'' width necessitated rolling up the edges of the sides to get them through and so the machine was later redesigned, increasing the width to 48'', which was agreed upon as the width necessary to take any side.

"The first machine of this design and size was put into operation in Peabody, Mass. about 1903 and is still in operation. This machine proved very successful

after a few strengthening changes.

"The introduction of presses into the operation of leather making was a slow process, with many obstacles and objections to be overcome. The side-leather manufacturers took it up first, finding the use of the press not only saved them money in the finishing process, but in many instances enhanced the value of the leather. The ability to emboss a design on the leather to cover any defects in the grain allowed them to put through skins that were hardly usuable before. It was not, however, until users started asking for plated leathers that the operation of smooth-plating in making leather became established.

"The smoothplating of calfskins and sheepskins started during the world war when leather was in great demand and quick deliveries were essential. The use of the press shortened production time and lessened production costs. With the war also came many poor skins, which could be covered up by embossing.

"At this time also came the call from sole-leather manufacturers for an extra heavy press with conforming head for smoothplating sole leather, bends, bellies, shoulders and heads. Smoothplating of this type of leather has not only been of great help in giving the tanner a firmer and flatter piece of leather with less bag, but has also allowed him to do away to a great extent with the operation of rolling.

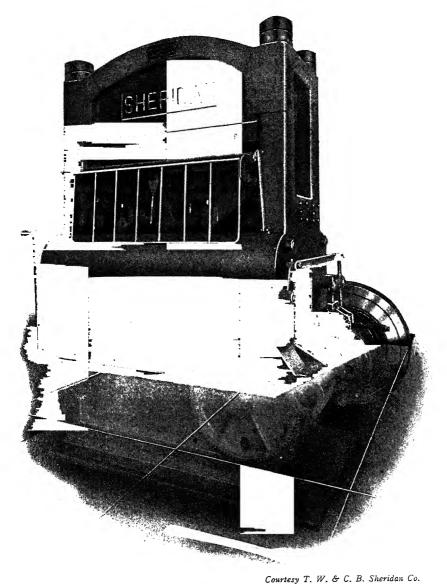


Fig. 376. Sheridan-8E Smooth-plating and Embossing Press, Showing Also Portion Submerged in Pit Below Floor Level.

"With the advent of embossed and fancy leathers for the shoe and pocketbook trade came the demand for heavier, stronger and more accurate presses. Sheridan presses are now being made in sizes up to 72"×36".

"Later came the demand for a press adaptable for both smoothplating and embossing, where the pressure exerted could be measured and automatically released when a certain predetermined pressure was reached, thus allowing the handling of light and heavy skins without changing the adjustment and doing away with the added expense of assorting the skins according to thickness. The Sheridan-9AH hydraulic resistance head press was brought out in 1938 to cover this demand."

Fig. 376 shows the Sheridan-8E press with a 48"×26" head, which is used for both smoothplating and embossing upper leathers. The temperature of the embossing plate is controlled by a heating chest equipped with inlets for both steam and cold water. Its enormous pressure of over 500 tons is easily controlled, if light ironing only is required, the pressure being regulated by a wedge operated by a handwheel within easy access to the operator's right hand.

The combination hand and foot treadle, enabling the operator to start the machine either with his left foot or left hand, leaves the right or both hands free to pull the leather forward and register it without loss of time. The safety guard on the operator's side is brought into action by starting the press. It consists of an iron-pipe frame hinged on the front of the machine on a level with the bed, which slowly rises upward and outward as the bed of the machine comes up, and pushes the operator away from the working parts of the machine. The friction clutch and brake enable the machine to be started quickly and stopped at any point in its operation.

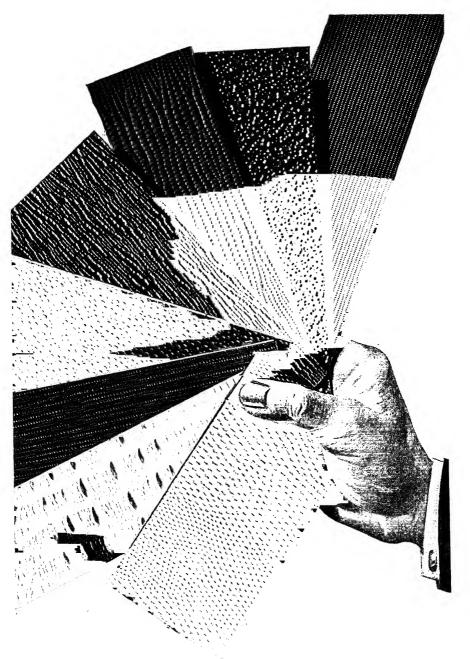
The press can be arranged either to throw off after each impression or to run continuously, as desired. The cam is arranged to give the maximum dwell on the impression, applying the pressure with a positive slow motion until it reaches the maximum, dwells and then releases quickly, the time under impression being about one-third of the cycle of the cam.

Building a Matrix for Embossing on a Sheridan Press

When the press is in operation, the embossing plate is locked face down into the fixed head of the press, which contains a steam heating chest for controlling the temperature of the plate. The leather is placed on a bed that rises to force the leather against the embossing plate, and then falls again. To get the best results, it is necessary to build upon this movable bed a matrix that conforms to the design of the embossing plate. There is a removable metal counter plate on the bed of the press which is used to hold the matrix. This counter plate should be bored and countersunk along it edges to take 136" stove bolts 3" long. By means of these bolts, attach to the counter plate a full-size sheet of heavy cardboard. Upon this, glue (with LePage's glue) a second sheet of cardboard, and upon this glue a third sheet. Then lock the counter plate onto the bed of the press, with the embossing plate in place, and run the press so that the cardboard is brought up against the embossing plate from 20 to 30 times, applying heat and pressure to get the impression well worked into the cardboard. Then let the cardboard remain in contact with the hot plate under light pressure until the glue has dried out, 60 to 90 minutes.

After the glue is dry, dampen the top board with a sponge with warm water and, while the board is still damp, operate the press 20 or 30 times with heat and pressure to obtain a sharp impression of the embossing plate on the board. Because the board dries out quickly under this operation, it may be desirable to dampen it again slightly while making the impressions.

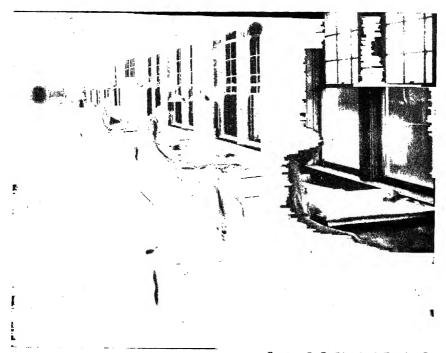
After the impression is well worked into the board, using flour-and-water paste, paste a sheet of matrix paper over the cardboard. Over this, paste a second sheet and then a third sheet, pasting each sheet on separately. Release the pressure on



Courtesy F. A. Ringler Co.

Fig. 377. Embossed Leathers Showing Various Designs.

the press so that the paper just kisses the embossing plate. Operate this way a few times until the paste dries out, but, as it is drying, increase the pressure and operate the press 20 or 30 times. If the paper should start to blister, release the pressure a little. Then emboss a thin sheet of paper and study it to note any low spots which may be either in the plate or in the matrix board. It is then necessary to build up these low spots with matrix paper until the design, upon embossing a sheet of paper, is uniform over the entire surface. After this is done, paste one or two sheets of matrix paper over the full area and proceed again as described above, releasing the pressure at first and then bringing it up to full pressure until the paper is dry. This is done to prevent the paper from sticking to the plate. If it should



Courtesy B. D. Eisendrath Tanning Co.

Fig. 378. Assorting and Grading Finished, Chrome-tanned Calfskins.

stick, it can be washed off with a damp cloth. If a very deep impression is desired, it can be obtained by using more matrix paper. After the matrix is thoroughly dry and ready for work, trim off the board front and back edges to match and sandpaper the edges lightly.

Embossing Plates

Embossing plates can now be obtained of great variety of designs. Calfskins can be made to simulate the skins of reptiles or of hogs, or given any one of innumerable designs. One of the pioneers in manufacturing embossing plates is F. A. Ringler Co., New York, who kindly furnished the cut of Fig. 377 showing various embossing designs on leather.

Smooth-plating

When it is desired to obtain a high gloss in smooth-plating, it is best to use a smooth plate of polished steel, either nickel- or chromium-plated. For dull finishes, it is best to use a polished brass plate. The proper building up of the bed is also very important to get the best results on various types of leather. For calfskins and sheepskins, it is best to have a rubber bed. Rubber beds or bolsters are made up of a special built-up rubber and are formed to fit the sizes of the different presses. Temperature and pressure controls are also very important for light skins.

In the first and second smooth-plating operations for buffed sides and splits, it is desirable to have a hard bed made of cardboard or hard felt. A matrix is built by bolting to the counter plate a sheet of heavy cardboard and then gluing onto this a second and then a third sheet of cardboard cut the same size as the smooth plate, but bevelled in with a smooth bevel about ½" all around. On this the felt is placed

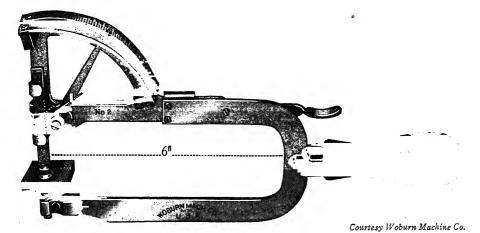


Fig. 379. Gauge for Measuring Thickness of Leather.

and bevelled all around about 4" to 1" smaller than the smooth plate. This bevel is to prevent plate marks on the leather. It is desirable to keep the felt clean by covering it with a sheet of kraft paper extending out and being attached to both back and front of the press.

If a rubber counter is used in place of the felt, this rubber which comes bevelled on all four sides, should be attached to the counter plate through the cardboards with stove bolts at the middle of both ends. This will keep the rubber from slipping without gluing. At least four thicknesses of a special kraft paper that will not crack should be used to cover the rubber.

Assorting and Grading Leathers

After skins have been completely finished, they must be assorted and graded according to quality. Fig. 378 shows a typical group of graders working on finished, chrome-tanned calfskins. Each grader is an expert in determining from the appearance and feel of a skin its value to the customer. He notes all grain damages, any unevenness of color, fineness of break, veins, graininess, tendencies for the grain to crack upon sharp bending, any tenderness in the leather, etc. He sums up all the

good and bad points of each skin, from which he determines whether the skin is to be classed as a first, second or third grade skin.

He also measures the thickness of each skin and grades it accordingly as a light, medium or heavy-weight skin. Usually a grader becomes so expert in this work that he does not need a gauge, but he keeps one handy to differentiate between borderline thicknesses. Fig. 379 shows the popular Woburn gauge often used both for finished leather and for leather to be measured at the splitting machine. The Turner gauge was shown in Fig. 264 (p. 446), and the description given there applies to both gauges. Fig. 380 shows another interesting picture of graders at work on chrome-tanned calfskins.

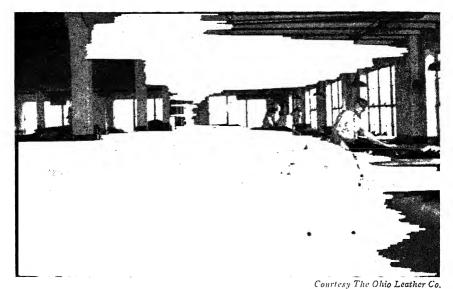
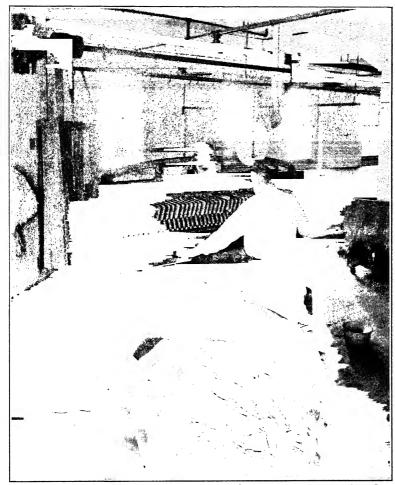


Fig. 380. Assorting and Grading Chrome-tanned Calfskins after Finishing.

Measuring Areas of Calfskins

Most light leathers are sold by area, the price per square foot being determined by the kind and grade of leather. In making proper deliveries and billings, it is very important that the tanner know the number of square feet of leather in each skin. Each skin is measured separately on a very ingenious measuring machine, one of which is shown in Fig. 381. There are many different types of measuring machine, but most of them work on the same general principle. When the machine is running and a skin is fed into it, it passes through under a series of notched wheels. These wheels rest on the leather and move as it passes through. Each is connected to a recording device and adds to the measurement shown on the dial only when leather is passing under it. If there are 10 such wheels to the linear foot, when leather passes under only one of them, the dial will record 0.1 sq. ft. for each linear foot of leather passing through. At a point where the leather is 3 ft. wide, 30 of the wheels will be moving and recording at the rate of 3 sq. ft. for each linear foot of leather passing through. In the 3-ft. width of leather passing through, if there should be a hole in the leather 6 inches wide, 5 of the 30 wheels will not record while passing over the hole. Thus in a very speedy and simple manner, the area



Courtesy A. F. Gallun & Sons Corp.

Fig. 381. Measuring the Areas of Finished Vegetable-tanned Calfskins.

of any skin is measured to an accuracy within 0.1 sq. ft. After a skin has passed through the machine, the operator has only to read its area from the dial and set it again to zero for the next skin. As soon as a skin comes through the machine, its area is marked on the flesh side to be used later by the checkers in recording the number of sq. ft. of leather going into each bundle.

Fig. 382 shows three measuring machines in use on the measurement of finished, chrome-tanned calfskins. A somewhat more detailed view of a measuring machine can be seen from the picture of the Woburn machine in Fig. 383.

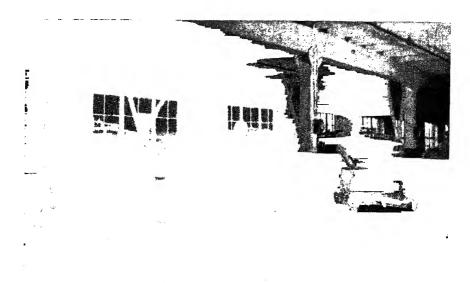
Checking and Bundling

After the skins have been measured, they pass on to a checker, who usually receives them in lots of one kind, weight and grade. As the skins are taken in lots

of 12 to be bundled together, he adds up the areas so that the bundle can be marked with the kind, weight, grade and area of the skins it contains. Fig. 384 shows the checkers and bundlers at work on finished, chrome-tanned calfskins.

In routine operations, leather is sometimes bundled before it is sold, and kept in a stock room, from which immediate deliveries can be made upon order. In such stock rooms, bundled leather is catalogued and filed like books in a library, so that any amount of any kind, weight or grade can be obtained without delay. Fig. 385 shows an ideal finished-leather stock room.

Fig. 386 shows a salesroom in which finished goatskins and sheepskins are graded and bundled. Customers can come into this room and select types of skins particularly suitable for their purposes. To the right are enclosed offices from which the business of the tannery is managed.



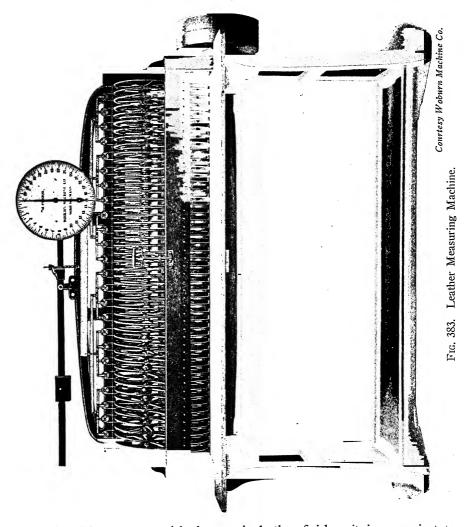
Courtesy The Ohio Leather Co.

Fig. 382. Measuring the Areas of Finished, Chrome-tanned Calfskins.

Raw Materials Used in Leather Finishes

The general subject of finishing all kinds of leather is one of enormous detail and many widely used commercial finishes are of secret composition, as a result of costly research on the part of finish manufacturers. If this entire volume were devoted solely to leather finishing, it would leave much untold. Dealing with the subject in a single chapter, it has seemed best to go into great detail first on only full-grain calfskins. Finishes that a tanner can prepare himself have been described and the mechanical operations involved have been given in as much detail as seems practical in the small space allowed. It is realized that this book will be used by tanners of many other kinds of leather and read by many who do not make leather at all. In the interest of clarity of presentation and the illustration of the fundamental principles involved, it has seemed best to describe the finishing of full-grain calfskins through to the point of delivery, then to describe the materials gen-

erally available for leather finishes, and then to give procedures for the finishing of many other types of leather, some of them involving the use of commercial finishes which many tanners purchase because they give results preferable to finishes which they themselves know how to prepare. Actually, the procedures given for calfskins can be applied with obvious modifications to any kind of leather with some degree of satisfaction. On the other hand, there are many excellent methods of finishing calfskins that are not included in the foregoing descriptions.



In describing raw materials for use in leather finishes, it is convenient to divide them into ten groups as follows: (1) protein materials; (2) gums and mucilages; (3) natural resins; (4) waxes; (5) pigments; (6) dyes; (7) antiseptics; (8) rubber latex; (9) pyroxylin and synthetic resins; and (10) miscellaneous materials.



Fig. 384. Checking and Bundling Finished, Chrome-tanned Calfskins.

Protein Materials

Casein is the most important protein material used in leather finishes, judging by quantity consumption. It is obtained from cows' milk by heating to 95° F., adding hydrochloric acid to reduce the pH value to 4.7, allowing the curd of casein to settle. decanting off the supernatant liquor, washing the curd repeatedly with water acidified to pH 4.7, and finally drying the purified curd. It is sold in the form of gray to white powder or crumbs. It does not dissolve readily in pure water, but if alkali is added to the water, it dissolves in considerable quantity. Tanners produce rather concentrated solutions of casein in water by adding aqua ammonia and boiling the solution. The casein dissolves in the form of an ammonium caseinate. When films of this are applied to solid surfaces and allowed to dry out, the ammonium caseinate dries to a tough transparent film. Upon drying at higher temperatures, the ammonia is driven off, leaving a tough film of casein that is not soluble in water. By incorporating finely ground pigments with the ammonium caseinate solution and then allowing a film of it to evaporate on a solid surface, the pigment remains firmly bound in the dried casein film. When films of casein are allowed to dry on leather surfaces, they adhere with great tenacity, and they hold pigments and other materials that were mixed with their solutions. reason, casein solutions are referred to as binders.

Milk has been found satisfactory as a finishing material because of the casein it contains. Actually milk contains only about 13 percent of solid matter, the rest being water. Of the 13 percent of solid matter, only 3 percent is actually casein; about 5 percent consists of sugars and nearly 4 percent fats, the remaining 1 percent

being albumins and salts. When milk films are allowed to dry on leather surfaces, they are not quite so hard as films of pure casein solution because the fats and other materials remain in the casein and *plasticise* it; that is, they keep it in a more plastic and less solid condition.

Egg albumin, as sold to the leather industry, is simply the dried whites of hens' eggs. The yolks are separated from the whites and the whites are then dried to a water content of about 15 percent; the original whites contain about 87 percent of water. The drying is usually done in shallow pans with the air temperature never exceeding about 100° F.; sometimes the drying is done in vacuum dryers at much lower temperatures, and a better product is thus obtained. The commercial

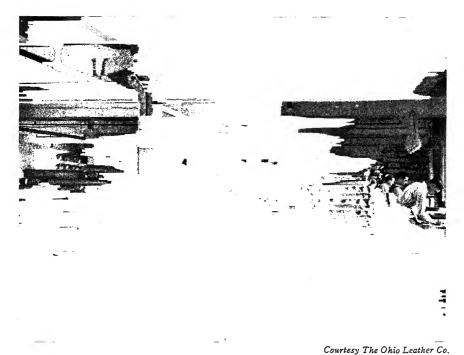


Fig. 385. Finished-leather Stock Room for Chrome-tanned Calf Leathers.

material is sold in chips or as a granular powder, containing about 16 percent by weight of water and about 60 percent of coagulable albumin. The dried albumin first swells when placed in cold water and finally dissolves to a turbid solution. Care must be taken not to heat albumin solutions above about 110° F., or coagulation may occur. When leather is coated with thin films of egg-albumin solution, they dry hard and glossy but the use of too much may produce on calf leather what has already been described as a *crusty break*. Like casein, egg albumin may be considered as a binder.

Blood albumin is the dried serum of the blood of cattle. The blood is allowed to clot and the serum is separated from the fibrin and corpuscles by centrifuging. The serum is then decolorized by treatment with animal charcoal, filtered and dried at

low temperature in vacuum dryers. It has many of the properties of egg albumin and is used in much the same way.

Ox blood consists of the whole blood of cattle and is much used in black leather finishes for leather that is to be glazed, such as glazed kid leathers. It is not much used on light-colored leathers because of its darkening effect, but for darker leathers the red corpuscles serve as pigment in covering many slight grain defects.

Gelatin is sometimes used in leather finishes. It is prepared largely from the trimmings of calfskins by dissolving in boiling water after a long liming and subsequent purifying process. It is sometimes obtained by extracting certain kinds of bones with boiling water. It is usually sold in thin sheets. It dissolves readily in

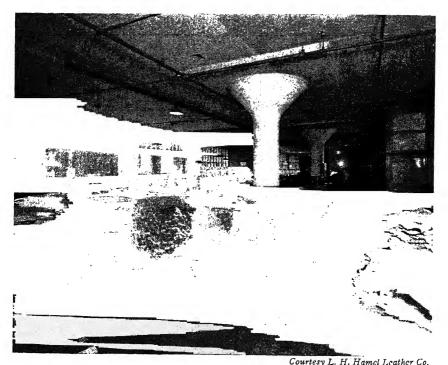


Fig. 386. Stock Room and Salesroom for Finished Goatskins and Sheepskins.

warm water and produces rather tough films on leather. Since these films are apt to be too hard, it is usually used with suitable plasticizers, such as glycerin or flax-seed mucilage. *Isinglass*, or fish glue, is a colorless, odorless and tasteless gelatin prepared from the inner skins of the swimming bladders of various fish, and is sometimes preferred to ordinary gelatin in making leather finishes.

Gums and Mucilages

The gums and mucilages used in leather finishes are exudations of plant cells of a carbohydrate nature. When soaked in water, they first swell by absorbing water and finally dissolve, usually very rapidly when the temperature of the water is raised to the boiling point. They are precipitated from solution by the addition of

alcohol. When used as a bottom finish on leather, they tend to cover uneven grain surfaces, and some of them reduce the luster produced by other finishing materials.

Algin is a mucilaginous material obtained from the common seaweeds Laminaria digitata and Laminaria stenophylla. The plants are first washed to remove salts and are then digested in a hot solution of caustic soda, which extracts the mucilaginous principle in the form of a salt, called sodium alginate. The free acid algin is precipitated by neutralizing the solution with sulfuric acid. The precipitated algin is added to a second portion of the alkaline extract in such quantity as to give a neutral solution of sodium alginate. Repeated precipitations with acid and redissolvings in alkaline solutions increase the purity of the material. A 10 percent solution of sodium alginate is used as a finishing material.

Irish moss is the dried plant Chondrus crispus, a seaweed found along the coasts of Ireland and New England. It grows on rocks that are periodically covered by the sea. It is collected at low tide and dried in the sun. It is sometimes called Iceland moss or Chondrus. The mucilaginous principle contained in the dried plant is called carrageenin, or carragheein, and is present to the extent of from 55 to 60 percent. The plant is washed with cold water to remove the salt and the mucilage is then extracted with boiling water for from 1 to 2 hours, enough water being used to give a solution containing from 4 to 8 ounces of dry mucilage per gallon. The dried residue will swell, if placed in cold water, and will dissolve in boiling water. A 1 percent solution will set to a jelly upon cooling. A 3 percent solution is a good emulsifying agent.

Flaxseed mucilage can be prepared by extracting ripe flaxseed (Linum usitatissimum) with about 40 times its weight of boiling water for one or two hours and straining while still hot. The mucilage is contained only in the outside shell. The extraction must not be unduly prolonged or the shells may be broken and much oil extracted along with the mucilage, which would be undesirable. A yield of about 6 lbs. of dry mucilage is obtained from 100 lbs. of seeds. When added to other finishes, it reduces their tendency towards brittleness and gives the grain a silky feel. The small amount of oil extracted with the mucilage assists in giving this effect. The mucilage stains readily with dyestuffs, being generally superior to starches in this respect.

Gum tragacanth is an exudation from the stems of the Astragalus gummifer and other varieties of Astragalus, which grow in Syria, Persia and other Asiatic countries. It is sold as dull, white, transparent plates or yellow powder. It swells in water, but dissolves upon the addition of alkali or hydrogen peroxide; alcohol precipitates it. It contains two substances, one resembling gum arabic and the other a substance insoluble in boiling water unless it is made alkaline. It has many of the properties of flaxseed mucilage and is actually to be preferred when used on leathers that are subsequently to be glazed. It is used in solutions containing from ½ to 1 percent of the dry mucilage.

Gum tragasol is obtained from the seeds of the locust bean, Ceratonia siliqua. The separated husks are ground and extracted with steam under pressure. Most of it comes from England and it is imported by John P. Marston Co. of Boston in the form of a stiff, opalescent jelly. Many tanners have found difficulty in dissolving it because even very dilute solutions form very stiff jellies. By heating it to the boiling point, it can be stirred. Water should then be added to it, very little at a time, while continuing to stir. After each small addition of water, no more should be added until that already added has been thoroughly incorporated. By continuing in this way, solutions of the desired strength can readily be obtained. As a finish, it has excellent filling properties, toughness, elasticity, resistance to

rubbing, and a remarkable binding power for pigments when applied to flesh splits. It is also used during tanning to impart a very desirable fullness and flexibility to leather.

Starches and their corresponding dextrins are used for some kinds of leather finishing, particularly for splits and for bag and strap leathers. Dextrins are made from corn, potato, or wheat starches by heating them to 482° F. and then pulverizing and are often called by various names, such as British gum, vegetable gum, artificial gum, gommeline, or starch gum. They dissolve readily in water, but are precipitated by the addition of alcohol. Where starches are used, they are first ground to a paste with cold water and then diluted with boiling water. Starches are usually preferred to dextrins because of their greater jelly-forming properties, but the dextrins can be dissolved much more readily. Sometimes glycerin is added to the starch mucilages to prevent stiffness or brittleness.

Natural Resins

Although shellac and rosin are not always classed among the natural resins, it is convenient to list them here to differentiate them from the synthetic resins.

Shellac, lac, or lacca is the resin most commonly used in making ordinary leather finishes. It is found as a thick excrescence on the small twigs of several species of East Indian trees and results from the bite or sting of the insect Coccus lacca. When collected and sold in this form, it is known as stick lac. It is first macerated with water in order to extract a brilliant red dye called lac dye. The seed lac is refined by melting and straining and then pouring in thin films over cylinders or plates and allowing to cool and harden. It is scaled off in thin flakes and sold as orange shellac. It is sometimes poured into molds to form button lac or garnet lac. White shellac is made by bleaching orange shellac with chlorine or sodium hypochlorite after first removing some of the waxes. Shellac consists largely of oxidized fatty acids.

Shellac is widely used in top finishes for glazed leathers where a hard, glossy and water-repellant surface is desired. It is insoluble in pure water, but dissolves readily in alcohol or in solutions made alkaline with ammonia or borax, which form water-soluble soaps with the oxidized fatty acids. The use of excessive amounts of shellac in finishes may result in a crusty break on the leather, but finish manufacturers vie with each other in producing plasticized shellac finishes free from this defect. They guard their formulas as trade secrets.

Colophony, or common rosin, is used to a limited extent in finishing leathers requiring a slight stickiness, such as those from which the grips of golf clubs are made. It is obtained by distilling off the turpentine oil from crude turpentine. It is a somewhat sticky red-brown to light-yellow solid which begins to soften at about 144° F. and melts at temperatures above 212° F. It is a very brittle solid with a glassy fracture and has a faint odor of turpentine, but very little taste. It is insoluble in pure water, but soluble in alkaline solutions and in acetone, alcohol, benzene, chloroform, carbon disulfide, ether, ethyl acetate, turpentine, and many oils and slightly soluble in petroleum spirits. It consists chiefly of abietic acid which can readily be neutralized by alkalies with the formation of water-soluble abietates or resin soaps.

Some tanners of chrome-tanned sole leather use rosin in their stuffing mixtures because it prevents the leather from becoming inordinately slippery when wet.

Waxes

Carnauba wax, or Brazil wax, is the wax most widely used in leather finishes and shoe polishes. It is an exudation from the leaves of the carnauba palm

Copernica cerifera, which grows in Brazil. It consists of hard, amorphous, yellow-green to light-yellow, brittle lumps. It is tasteless and has a peculiar, agreeable odor. It is insoluble in pure water, but watery emulsions of it can readily be made by melting it and pouring the molten mass into boiling soap solutions while stirring vigorously. Carnauba wax is graded according to color and uniformity by numbering 1, 2 and 3, number 1 supposedly being the finest grade and lightest in color. Grades 2 and 3 include the varieties labelled "North Country" and "Chalky," which have a greenish to greenish-gray cast. Bleached or white carnauba wax is obtained by adding paraffin wax and treating the melted mixture with hot, dilute, alkaline solutions. The unsaponified portion, which floats on top, is pumped off, clarified with some adsorbing agent, filtered, and then allowed to cool and solidify. The byproduct remaining in the alkaline solution is recovered by acidifying the solution and collecting the precipitate, which is used for certain kinds of shoe polish. The popularity of carnauba wax is due to its hardness and relatively high melting point. It is applied to leather as a dispersion in soap and water. It gives a very high shine to leathers which are brushed, but not glazed. Glazing raises the temperature of the finished surface of leather to a point higher than the melting point of any wax, which sometimes causes wax finishes to dull. Dispersions of carnauba wax are used in shoe factories to give the shoes a fine luster before they are sent to the market.

Beeswax is obtained from the honey-comb of the common bee, Apis mellifica, and some allied species. The pressed honey-comb is melted in hot water, drawn off into molds, and bleached by exposure to sunlight or to chemical oxidizing agents. It has a faint, characteristic taste and a honey-like odor.

Although it is insoluble in water, fine and stable emulsions can be made by stirring the molten wax into boiling soap solutions. Because of its softness and low melting point, leather finished with it is easily married by fingering.

Japan wax is obtained from the berries of three varieties of Rhus, growing in Japan: Rhus succedanea, Rhus vernicifera, and Rhus sylvestris. The berries are ground to a meal and the wax extracted by heating with steam and pressing, repeatedly. It is bleached in the sunlight. It is insoluble in water, but soluble in benzene and naphtha. It is dispersed by alkaline or soap solutions.

Because it is a soft wax and leather finished with is easily marred by fingering, it is not widely used in leather finishing, but it is widely used in shoe polishes because it can be rubbed to a high luster with very little friction.

Candelilla wax is found as an excretion on the desert plants along the United States-Mexican border, and is extracted by boiling water. It is a hard, brittle, translucent, dark-brown wax which gives off an aromatic odor when heated. It is insoluble in water, but is dispersed by alkaline or soap solutions. It dissolves in hot alcohol, ether, acetone, chloroform, carbon disulfide, oil of turpentine, or gasoline; but, upon cooling, the solutions become pomade-like masses. Its hardness and high melting point place it in the class with carnauba wax rather than with the softer beeswax and Japan wax.

Montan wax is sometimes used in place of carnauba wax. It is a bituminous substance extracted by various solvents from the pyropissite obtained from the lignites of Saxony and Thuringia at a temperature of about 480° F. and 50 atmospheres' pressure. It is a hard, white, odorless wax melting between 170 and 190° F., or about the same range as that for carnauba wax.

Pigments

Many leather finishes contain insoluble mineral pigments or lakes finely ground in oil. Being opaque, they tend to hide defects in the grain of the leather,

making the color and general appearance more uniform. Pigments for lacquers are usually ground in one of the oils or plasticizers to be used in making up the lacquer, but for water finishes it is customary to grind the pigment in a sulfonated oil. The surfaces of the particles of pigment become coated with the sulfonated oil which gives them an attraction for water that keeps them in suspension when mixed with water or with watery finishes.

When grinding pigments in sulfonated oils, it is desirable to use the minimum amount of oil that will do the work, because excessive amounts of sulfonated oils in leather finishes may prove undesirable. The finer the degree of subdivision of a pigment, the greater its surface area per pound. In grinding pigments, it is desirable to know approximately the minimum amount of oil required for the different pigments available on the market. Working in the writer's laboratories, W. Varo determined these amounts for a number of different commercial pigments used in leather finishes. The results are given in Table 48.

Table 48. Minimum Amounts of Sulfonated Cod Oil Required to Grind Various Common Pigments Used in Leather Finishes.

			bs. oil 100 lbs.
Color	Commercial name		igment
White	titanium oxide	titanium dioxide	120
White White	blanc fixe lithophone	barium sulfate barium sulfate, zinc sulfide	35
Yellow	lemon chrome yellow	lead chromates and sulfates	60 35 34 35
Yellow	medium chrome yellow	lead chromate insoluble aniline dyes	35 206
Yellow Orange	toner yellow orange chrome yellow	basic lead chromate	200
Orange	raw sienna	iron, manganese and aluminum oxides and silicates	123
Red-brown Brown	burnt sienna burnt umber	iron, manganese and aluminum oxides and silicates iron, manganese and aluminum oxides and silicates	93 115
Brown	Van Dyke brown	copper ferrocyanide	100
Brown	toner brown	insoluble aniline dyes	254
Red Red	para red Indian red	paranitrobenzene-azo-betanaphthol iron oxide	125 25
Green	chrome green	chromic oxide	25 35
Blue Blue	ultramarine Prussian blue	sodium and aluminum sulfide and silicate ferric ferrocyanide	70 118
Black	magnetic oxide	iron oxides	70

Practically any of the sulfonated oils used in the tannery can be used for grinding pigments for leather finishes. Pigments can also be ground in casein finish. It is sometimes advantageous to make up a finish without pigment and then to grind the pigments in it.

Although many of the mineral pigments are mined as such, many are produced chemically. In recent years, there has been a tremendous development of organic pigments, which really are insoluble aniline dyes. They have the advantage of constancy of composition and the colors available cover practically the entire range of the visible spectrum, but are likely to be less light-fast and are more likely to bleed and to crock.

Gold and silver effects are sometimes produced by using finely divided powders of aluminum metal in lacquer binders; they are made to appear like gold simply by incorporating yellow and orange lacquer-soluble dyes with them. The best of the gold and silver leathers are finished by covering them with pure gold and aluminum leaves, an operation described later in this chapter.

Beautiful iridescent pearly effects are produced on leather by the use of the crystalline guanine obtained from the scales of fishes such as the herring, shad and pilchard. About one pound of pearl essence is obtained from 200 lbs. of fish scales. The material is marketed by Paispearl Products, Inc., of New York under the name of *Paispearl Genuine Pearl Essence*. The writer has made much beautiful pearl leather with it by incorporating it into lacquer and applying it as

a top coat to finished calf leathers. Other suppliers of pearl products are The Mearl Corp., New York, Hudson Pearl Co., Inc., Union City, N. J., and Givaudan-Delawanna Inc., New York.

Dyes

Aniline dyes are used extensively in leather finishes to make the final adjustment of color to the exact shade desired. A finishing-room foreman usually keeps freshly prepared dye solutions of a great variety of colors on hand at all times to make these adjustments. He soon learns what dyes are compatible with each of his various finishes. When he is using neutral or faintly alkaline solutions of casein, he usually limits himself to acid dyes, because basic dyes and alkaline casein precipitate each other.

When solutions of acid dyes are mixed with solutions of basic dyes, the dyes combine chemically and precipitate out as a water-insoluble *lake*. Many of the insoluble dye pigments are made in this way.

Extensive use is made of the tendency for acid and basic dyes to combine with each other to form insoluble lakes. Before finishing, it is common to apply to the leather a coat of an acid dye, allow it to dry, and then apply a coat of basic dye. The insoluble lake formed has a measurable degree of covering power (hiding power), and the leather may be made to appear much more uniform in color without the use of mineral pigments. As a rule, the basic dyes give the leather more intense and brilliant colors, but they are not so fast to light as the acid dyes.

The use of wax-soluble dyes in making carnauba-wax emulsions has already been described. Special dyes soluble in lacquer solvents are available for use with lacquer finishes.

Antiseptics

Casein solutions and many of the other solutions used in leather finishes are so readily putrescible as to require the use of antiseptics unless they are to be used up immediately after being made. However, some antiseptics react chemically with finishing materials so that their antiseptic value is lost. Before attempting to use any new antiseptic, its value must be proved under the conditions under which the finishing materials are kept, which is a very simple matter for any finishing-room foreman. Among the popular antiseptics for leather finishes are certain essential oils, phenolic compounds and compounds which liberate chlorine in solution.

Although *phenol*, often referred to as carbolic acid, is not much used in leather finishes, antiseptic power is often determined and recorded in terms of the antiseptic power of phenol.

Working in the writer's laboratories, W. Varo studied the effect of various antiseptics upon a solution containing \(\frac{1}{2} \) lb. of casein per gal. at pH values from 7.1 to 7.4 and at a temperature of about 77° F. To this finishing solution, he added various amounts of different antiseptics and then noted the lapse of time before putrefaction became noticeable, as determined by the occurrence of foul odor. With no antiseptic, it usually became foul after standing over night. With 1 part of phenol per 1000 parts of finish, the finish remained sweet for 7 days; with 2 parts per 1000, it remained sweet for 40 days and with 4 parts per 1000, it was still sweet after 2 months. Sodium phenolate, creosote and sodium salt of creosote showed essentially the same antiseptic power as phenol.

Betanaphthol alone is not very soluble in water, but it can be dissolved as a

sodium salt by mixing it with one-fourth its weight of caustic soda, or it can be emulsified in water by mixing it with one-half its weight of soap. When emulsified with soap, 1 part kept the finish sweet for 20 days and 2 parts kept it sweet for more than 2 months. But with the sodium salt, ½ part kept the finish sweet for 1 month and 1 part for more than 2 months. The sodium salt of betanaphthol is thus about 4 times as powerful as phenol.

Collatone was found to have practically the same antiseptic power as the sodium salt of betanaphthol. In the same category belong also paranitrophenol, the Dowicides (Dow Chemical Co.) and the Santobrites (Monsanto Chemical Co.).

Under the same conditions, Varo also determined the antiseptic powers of various essential oils. These were made into solutions or dispersions in two different ways. In one way, they were dissolved in alcohol to make 10 percent solutions, and in the other they were mixed with 4 percent sulfonated castor oilsoap solutions to make 10 percent solutions of the essential oils. These were added to the casein solutions to give the proportions of dry antiseptic to casein solution shown in Table 49, which shows the number of days the finish remained sweet after the addition of the essential oil. Parallel tests were run with phenol in order to get values comparable with values available in the literature on the antiseptic values of other substances based on that of phenol as unity.

Table 49. Preservative Action of Various Essential Oils upon a 4% Solution of Casein at 77° F. and pH Value of 7.3.

(Values given in number of days that the finish remained sweet)

Essential		Parts oil per 1000 parts of finish										
oil	0.25	0.50	1.00	2.00	3.00	4.00	5.00	6.00	8.00			
Phenol in alcohol	2	4	4	70	120	120	1 <i>7</i> 0	170				
Oil of sassafras												
In alcohol	4	4 5	4 7	б	6	7	25	28	29			
In alcohol In soap solution		5	7	7	13	13	16	25	30			
Oil of eucalyptus												
In alcohol	2	3	3	6	7	8	24	24	25			
In soap solution	4	4	5	8	16	16	24	24				
Oil of mirbane												
In alcohol	4	4 5	5	8	16 51	16 51	35	38				
In soap solution	3	5	5	20	51	51	<i>7</i> 0	<i>7</i> 0				
Oil of thyme									over			
In alcohol	3	3	16	23	62	65	120	120	163			
Thymol in alcohol	4	7	9	20	100	over	over	over				
THYMEOT III AICOHOL	4	,	2	20	100	1 7 0	170	1 <i>7</i> 0				

Oil of thyme is the most effective preservative of the essential oils studied. It is obtained by distillation from the leaves and flowering tops of the Thymus vulgaris, grown principally in the mountainous regions of southern France. It is a yellowish-red liquid with a strong odor of thyme, an aromatic, pungent, cooling taste, specific gravity of 0.905 to 0.950; it is soluble in alcohol, ether, chloroform, and carbon bisulfide and very slightly soluble in water. It contains thymol, carvacrol, cymene, linalol, and borneol. Thymol, isopropyl-m-cresol, is prepared from oil of thyme by treatment with caustic soda and decomposition of the sodium salt with hydrochloric acid. It consists of colorless crystals, has a specific gravity of 0.979, melting point of 110° F., and boiling point of 450° F. It is soluble in water to the extent of about 3 parts per 1000, but is much more freely soluble in alcohol, carbon bisulfide, chloroform, oils, and ether.

Oil of mirbane, or artificial oil of bitter almonds, is nitrobenzene. It consists of bright yellow crystals or yellow oily liquid with odor and taste of bitter

almonds. It has a specific gravity of 1.199, a melting point of 48° F., and a boiling point of 412° F. It is slightly soluble in water, but freely soluble in alcohol and ether. It is poisonous.

Oil of eucalyptus is obtained by distillation from the fresh leaves of many species of Eucalyptus. It is a colorless or faintly yellow liquid with a characteristic aromatic odor and spicy, cooling taste. It has a specific gravity of 0.85 to 0.94. It is slightly soluble in water, but more freely soluble in alcohol, chloroform, carbon bisulfide, and ether. It contains phellandrene, cineal, citral, pinene, and terpenes.

Oil of sassafras is distilled from the roots of the Sassafras officinale, native of North America from Canada to Mexico. It is a yellow to reddish-yellow, volatile liquid with a pungent, aromatic odor and a warm, aromatic taste. It has a specific gravity of 1.065 to 1.095. It is slightly soluble in water, but freely soluble in alcohol, chloroform, carbon bisulfide, ether, and glacial acetic acid. It contains safrol, eugenol, camphor, pinene, and phellandrene.

Rubber Latex

In finishing heavily buffed leathers and splits, there is need for a material that will fill the spaces between the fibers. Some tanners accomplish this by using large amounts of casein binder and pigments. Many tanners incorporate with these finishes considerable amounts of rubber latex, which gives the leather a smooth and elastic surface. Rubber latex has been much used to advantage in the manufacture of both smooth and embossed leathers. Because of its tendency to produce a coarse break in the leather, it is rarely used on the finer, full-grain leathers. It is a sticky, milky juice secreted by various species of rubber trees. It is not a sap, but a juice secreted to aid in healing damage to the tree. It is an emulsion of finely divided rubber in a faintly alkaline solution and is coagulated by making the solution faintly acid. It contains about 33 percent of rubber and has a pH value of about 7.2. It is usually added to finishes made faintly alkaline with ammonia.

Synthetic rubbers can be applied to leather with results that are satisfactory except for the disagreeable odor that they impart. The writer has finished some very fine leathers with solution of synthetic rubber, but they had a disagreeable odor that would fill an entire room in which they were kept. It seems probable that this objection will be overcome and that the synthetic substances will either take the place of or actually supplant natural rubber latex in leather finishes.

Pyroxylins and Synthetic Resins

Pyroxylins are cellulose nitrates made by treating cellulose, in the form of paper, wood-pulp, or cotton, with nitric and sulfuric acids. When cotton is given the maximum degree of nitration, the product is gun-cotton, which contains over 12.5 percent of nitrogen. This is not soluble in the ordinary lacquer solvents. The pyroxylin used in making lacquers is a rather indefinite series of cellulose nitrates containing from 11.0 to 12.5 percent of nitrogen. After the cotton has been treated with the mixed acids, it is centrifuged to remove the bulk of the acid, after which it is washed in boiling water, then pulped, and the adhering water is finally displaced by alcohol. Since it is dangerous to transport dry pyroxylin, it is usually sold and shipped mixed with about 30 percent by weight of alcohol. Pyroxylins are graded according to the viscosity of their solutions made up under fixed conditions. The viscosity is usually recorded as the number of seconds required for a standard ball to fall through a definite column of the solution. Pyroxylins are referred to as "half-second cotton," "60-second cotton," etc., accord-

ing to the viscosity as measured by the falling-ball method. Pyroxylin has a specific gravity of about 1.6. It is practically insoluble in hot or cold water, naphtha, or carbon tetrachloride; it gelatinizes, but does not dissolve readily in alcohol. Acids have but little effect upon it, while alkalies and alkali sulfides attack it vigorously. Sunlight causes deterioration of pyroxylin, but this is overcome to a large extent in practical use by the incorporation of opaque pigments which absorb the harmful ultraviolet rays and permit the lacquered surfaces to withstand the action of sunlight for years.

Commercial lacquers usually consist of pyroxylins dissolved in pyroxylin solvents, such as amyl acetate or butyl acetate, to which may be added cheaper diluents, such as benzene or toluene; plasticizers, such as castor oil or dibutyl phthalate; gums and resins, such as ester gum or shellac; anti-blushing materials, such as butanol or diacetone alcohol; and pigments and dyes. After a coat of lacquer has been applied to a leather surface, the solvents and diluents begin to evaporate and the film gradually sets to a jelly. If this jelly film is clear at the time of setting, it will finally dry out with a high luster. However, if any of the lacquer ingredients precipitate before the film has set to a jelly, the dried film will become cloudy, a condition known as blushing. Water absorbed from the atmosphere on a damp day may cause precipitation and blushing. Anti-blushing materials are simply materials which prevent such blushing when added to the lacquer. Plasticizers are simply materials which keep the pyroxylin film from becoming too hard after the solvents have evaporated.

Lacquers have been used as finishes for leather with very beautiful effects, and to some extent have replaced linseed-oil varnishes in the final coating of patent leathers. Among the chief difficulties encountered with lacquers for finishing leathers have been lack of adhesion to the leather, with consequent peeling, and the absorption of the plasticizers by the leather, leaving the film very hard and causing a coarse break in the leather.

One of the most successful uses of lacquers on shoe leathers has been as a top finish, where only an exceedingly thin coat is applied after the regular finishing. Such lacquers, when prepared properly, permit the leather to be glazed with very satisfactory results. One of the formulas developed in the writer's laboratories is as follows:

Finish No. 16 (glazing lacquer finish): Dissolve 84½ lbs. of pyroxylin (15-second cotton mixed with 30 percent weight of alcohol) in 61½ lbs. of amyl acetate and add in succession, while stirring, 10 lbs. of castor oil, 29½ lbs. of ethyl acetate, 31¾ lbs. of butanol, 84½ lbs. of toluene and 52¾ lbs. of alcohol denatured by Government formula No. 23A. This makes a lot of approximately 50 gals. This is applied with a spray gun to the dry leather after all other finish has been added. It is thoroughly dried and the leather is then glazed and staked.

To this finish, it is possible to add *Paispearl* to get beautiful pearly effects, aluminum powders to get metallic effects, and lacquer-soluble dyes with either pearl or aluminum.

Many of the early difficulties with lacquers as leather finishes have been overcome by the development of improved plasticizers and by the use of synthetic resins. Since the firm of Röhm & Haas Co., of Philadelphia, has been a pioneer in the development of both lacquer and synthetic-resin finishes for leather, the writer has asked Mr. H. B. Walker of this company to provide a brief resumé of the developments of the past decade, which is reproduced below:

"From the point of view of gallonage consumption, the water pigment finish—made essentially from protein materials, natural resins, gums, and waxes, com-

bined with dispersed pigments and dissolved dyestuffs—still holds first place in the leather industry. The greatest single factor responsible for this is undoubtedly the low cost of these materials, but in addition, they have a number of desirable technical features, chief among which is the ability to be glazed with ease and to preserve the characteristics of the tanned skin without alteration.

"The only change in this type of finish, from the technical or development standpoint, during the past decade, has been the use of water dispersions of synthetic resins, chiefly the acrylic ester polymers, which are described below, as binding and film-forming materials in addition to those customarily employed. These materials confer the advantages of increased leveling, filling, adhesion, and flexibility, in addition to improving the permanence of the flexibility. The amounts of these materials used as additions to the customary protein and other binders vary greatly with the leather, and are generally determined by the limit of workability or the limit of cost.

"The type of finish other than the water pigment finish which is most extensively used in the leather industry is, of course, the lacquer finish. The origin of lacquer goes quite far back, the earliest patent on a composition suitable for coating leather, of which I know, being a British patent issued in 1855.

"A fair amount of work was done with these lacquer finishes, or dopes as they were called, on upholstery leathers and in making splits of one kind or another. The real impetus to the development of lacquer finishes, however, came in the post-war years and as the result of a purely war-time development. Prior to World War No. 1, solvents suitable for use in commercial lacquers were relatively scarce and expensive. The war demand for acetone produced the acetone fermentation process, of which butanol was a large by-product. This butanol, combined with acetic acid, yielded butyl acetate at a cost previously unrealizable and made practical lacquers commercially feasible. This in turn brought on the development of the low-viscosity type of nitrocellulose which gave a tremendous fillip to the then adolescent lacquer industry, by making possible the production of lacquers which could be used for wood and metal coatings. This again intensified the development work on new and improved solvent materials, so that shortly there became available to the lacquer manufacturer a wide range of materials at prices which made their utilization economically feasible.

"In the midst of all this rapid development of lacquers in general, the idea of using lacquer finishes on leather, where the water-proofing qualities in particular looked especially attractive, evolved naturally, and the lacquer finish for the leather industry, as distinct from the nitrocellulose dope of the early dope split years, came into being. It is interesting to note that, on account of the circumstances surrounding the historical development of the water pigment finish, in Europe and most other parts of the world, the lacquer finish preceded the development of the water pigment finish, whereas in America the reverse sequence occurred, and the lacquer finish followed the pigment finish.

"The early efforts to develop lacquer finishes suitable for leather borrowed the ideas and techniques of the then young lacquer industry as a whole, which was directed mainly toward wood and metal finishes. The first results were disappointing, and we came very quickly to the realization that an entirely new approach would have to be tried. The first stumbling block was the question of flexibility, and the second the question of retaining what flexibility we did have. It came to be realized very early that the word flexibility from the standpoint of wood and metal finishing, and from that of leather finishing, has two entirely different mean-

ings; what is flexible in the metal lacquer is anything but flexible in the leather lacquer.

"It is advisable in this connection, to examine what we mean by 'flexibility.' Usually the word simply means 'ease of being bent'; but, as commonly used in its application to a thing like a leather finish, it has a much wider meaning. What is really required in the finishing material applied to most kinds of leather is the ability to stretch without breaking, and to withstand repeated stretching without breaking. I think this distinction is important, because there are many things which, while in themselves flexible, would be entirely unsuitable for use as a coating on a piece of leather. A sheet of paper, for example, is flexible in the usual sense of the word, yet a finish producing a film with the properties of a piece of paper would be, of course, quite worthless as a leather finish.

"The greatest difficulty, however, was that we could not even hold on to the little bit of flexibility we did have. At that time, the only plasticizers that were known were relatively mobile materials of a more or less oily nature. Everyone who has worked with leather knows the terrific appetite that leather fibers, particularly vegetable-tanned leather fibers, have for any oily material. Early plasticizers for lacquer finishes proved to be no exception, and were quickly robbed from the finishes by the leather itself, so that, while passable at the time of application, they lost flexibility very rapidly.

"Another great early difficulty was lack of adhesion. Nitrocellulose itself does not possess very much of what I may, for lack of a better term, call specific adhesion; in most cases, the greater the amount of plasticizer used to get flexibility, the less the adhesion becomes. This is of course a most unfortunate state of affairs, but one hard to remedy. The adhesion difficulty was particularly in evidence on chrome leather. As most shoe leather is chrome leather, the lack of adhesion was right on the spot where it would show up most and cause the most trouble.

"This brief history gives a general idea of the status of the lacquer finish in the early stages of its development, say some twelve or fifteen years ago. The finishes had rather poor flexibility, in the special sense in which I have defined flexibility, the flexibility did not last, and the finishes did not stick to the leather, except on occasions which could never be predicted.

"I need not dwell in detail on the intervening period during which the lacquer finishes, and their very youthful first cousins, the synthetic-resin finishes, have been developed to the point where they are practical, usable, materials, free from most of the drawbacks of their predecessors. Most of the progress has been accomplished through the medium of research, to use a word that has recently been very much abused. This research turned up plasticizers which were effective in imparting a high degree of permanent flexibility, and the development of synthetic resins largely overcame the adhesion difficulty, in addition to taking care of some other troublesome points.

"Lacquer finishes today are plasticized mainly with flexible synthetic resins, either alone or in combination with 'solvent' plasticizers. They are generally marketed in the form of clear solutions, containing both nitrocellulose and plasticizer, in properly balanced solvent mixtures, plus suitable colors and thinners.

"The binders and colors are mixed in the proportions found by experience to be most suitable for the leather being finished, and are then thinned with the appropriate thinner. Application is mainly by spray, although hand swabbing may be used for the first coat, and the number of coats may vary from one to five or six, depending entirely on the type of leather and the effects desired.

"In addition to the cellulose derivative most used in lacquer finishes, namely

nitrocellulose (or, more accurately, cellulose nitrate) other cellulose derivatives are used. Of these may be mentioned the acetate, which is actually employed in fair amounts for special applications, the acetopropionate and the acetobutyrate. The last two are relative newcomers to the field and so far have found no particular application, but their use may develop.

"The cellulose ethers have been proposed for use and have met with little acceptance. This is not because they do not possess desirable properties, but because they also possess concomitant drawbacks which more than offset their advantages. It has to be emphasized that it is not so much any single property of a material which determines its use as a desirable combination of properties.

"Chlorinated rubber has been proposed as a leather finishing material, and plastics such as that made from polyvinyl chloride also have a limited application.

"Although lacquer finishes, by themselves, made considerable progress in the industry, and are still used alone in some cases, most finishes today are combinations of lacquers and acrylic resins, the resins being used as priming coats for the lacquer. A few kinds of leather are still finished with lacquers only, but they are of minor importance.

"The acrylic ester polymers are, of course, not new. Many efforts have been made, over a period stretching back twenty years or more, to utilize solutions of

such polymers in organic solvents as leather coating compositions.

"The resins of this type possess high specific adhesion, and high flexibility which is inherent in the material and not imparted to it by the addition of mobile plasticizers. Polymers of the vinyl esters give similar products which have, however, been found to be less suited to the particular requirements of leather coating.

"The great drawback of the acrylic ester polymers is their very thermoplastic nature. This is a characteristic of this type of polymer, and much effort has been expended to overcome or minimize it. Some success has been attained, but not by any means as much as is desirable. More research is required here.

"In spite of their high inherent flexibility, these materials met with no particular success until a process was evolved for preparing them in the form of water dispersions. Such water dispersions have unique properties which happen to be particularly adaptable to the problems involved in leather finishing. Some of the properties arise from the nature of the resins themselves, and others from the fact that they are in the form of water dispersions.

"The question of the behavior of water dispersions in such applications is sufficiently important to merit some consideration. The most familiar substance of this type is, of course, rubber latex, which is a naturally occurring water dispersion of a plastic material. The advantages and disadvantages of rubber latex as a component of water finishes are well-known and need not be discussed here.

"One of the biggest problems of leather finishing, if not the biggest, is to finish imperfect leather. It has been often emphasized to me that anyone can finish good leather; the trick is to finish poor leather and make it look good. Natural imperfections in and damages to hides and skins are almost universal, and the total amount of perfect stock available for leather-making purposes is negligible from the tanners' point of view. This brings up the big point in any leather finishing process, that the principal need is to cover, or at least minimize, grain and other defects. Thanks to what we like to call the perversity of nature, it happens that most leather finishing processes seem to emphasize rather than minimize the irregularities that occur, and it is here that the water dispersions score. Because of the fact that they dry by coagulation rather than by evaporation, they possess the very excellent property of filling up low spots without building up on the good

spots, so effecting a general leveling which is most desirable. This is something for which the chemist can take no credit at all. It is simply a property of these materials of which advantage has been taken, and was not put there by design on the part of anyone.

"The idea of using water dispersions or emulsions has been tried in other directions. One of the rather obvious things to do is to emulsify lacquer, and much work has been done along this line, the earliest patents going back many years. Emulsified lacquers have been used to some extent for coating purposes in the leather industry, but these also suffer from very definite drawbacks which have not, to date, been entirely overcome."

Miscellaneous Materials

In addition to the materials described above for all kinds of finishes, many more are used, of which the more important will be mentioned. All kinds of sulfonated oils are employed, both directly and as dispersing agents for pigments. Various soaps are used, both directly and as emulsifying agents for waxes and for antiseptics. Alcohol, fusel oil and aniline are sometimes used as solvents and as antiseptics.

Diethylene glycol is used as a plasticizer in all kinds of water finishes to prevent the dried coat of finish from becoming too hard or brittle. Glycerin is also employed for this purpose.

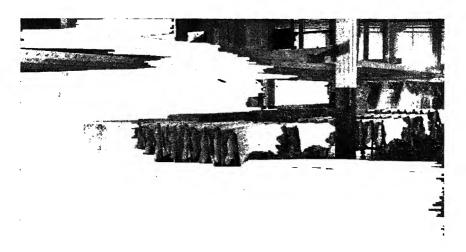
Perfumes, such as birch oil, civet, musk, styrax, benzoin, patchouly and sandal-wood oil, find a use in finishes for special purposes where odor is an asset. Birch oil is applied to Russia calf leather to give it the birch-tar odor characteristic of the original Russia calf leather which was tanned in Russia with birch bark. Birch oil is obtained by dry distillation of the bark and wood of the *Betula alba* and further rectification by steam distillation. It is a limpid, dark brown, poisonous liquid with a penetrating odor. It has a specific gravity of 0.886 to 0.950. It is very slightly soluble in water, but is freely soluble in naphtha, benzene, chloroform, ether and alcohol.

Finishing Miscellaneous Leathers

The procedures given for finishing both chrome-tanned and vegetable-tanned calf leathers were for full-grain leathers. When leathers are buffed deeply, they not only absorb more of the finishing materials, but they require more to fill up the voids between the cut fibrils of the grain surface. For side leathers, they require very much more pigment to hide irregularities; and more binders must also be used to carry the pigment, or it will not adhere to the leather. The rules given for finishing chrome-tanned calf leathers can be applied to buffed side leathers, but the quantities used must be increased, particularly on the bottom coat, and it may be found desirable to add rubber latex or water-dispersed acrylic resins to the bottom coat containing the pigment.

In describing the finishing of leather, once it becomes necessary to depart from a standard leather, such as a No. 1 quality, full-grain calfskin, much must be left to the judgment of the finishing-room foreman, who must have skill, experience and good judgment in determining what changes may be required to get the best results on stock of varying characteristics. Certainly no rigid procedure can be laid down that will give the best possible results on every class and grade of stock. All that we can hope to do in this chapter is to illustrate general principles that will assist a finisher to arrive at the best procedure for any kind of stock with as little delay as possible. For a skilled finisher, this is not nearly so difficult as it might seem

from this description. After a finisher has been given descriptions of the available materials and their uses under definite conditions, he can, with sufficient experience, apply them under almost any conditions. The balance of this chapter will be devoted to giving general formulas for finishing many different kinds of leather many involving the use of commercial finishes of secret composition. These will be far from complete, but it is believed that they will be very helpful to finishers in arriving at satisfactory procedures for finishing the various leathers that must pass through their hands. In the selection of these procedures, the writer acknowledges the kind assistance of Röhm & Haas Co. of Philadelphia, C. L. Hauthaway & Sons of Lynn, Mass., K. J. Quinn & Co. of East Boston, Mass., Apex Chemical Co. of New York, and Kepec Chemical Corp. of Milwaukee.



Courtesy The Ohio Leather Co.

Fig. 387. White-leather Department of Calfskin Tannery.

White Leathers

For full-grain white leathers, an excellent white finish can be made from maxwhite paste, the manufacture of which is described in Chapter 15 under the heading "Fatliquoring White Leathers."

Finish No. 17 (white): Mix 7½ gals. of Finish No. 1, 2 gals. of Finish No. 3, 77 fl. oz. of diethylene glycol and 4 fl. oz. of sulfonated linseed oil. Mix intimately with this 118 lbs. of maxwhite paste.

Finish No. 18 (white bottom coat): To make 1 gallon: To 1 lb. of Finish No. 17, add 12 fl. oz. of Finish No. 1, 20 fl. oz. of Finish No. 1a, 2 fl. oz. of Finish No. 3 and water to make 1 gallon. Mix well and strain through cheese-cloth for use.

Apply to the grain side of the white leather 4 light coats of Finish No. 18, drying after each coat. After drying after the fourth coat, roll twice around, brush twice around and stake. Then dry very thoroughly and apply a very light coat of

Finish No. 16 with a spray gun, and the leather is completely finished. If the effect is preferred, add a small amount of white pigment to Finish No. 16 before applying.

It is so very important to keep white leathers clean during the finishing operations that they should be kept in a room or department by themselves. Fig. 387 shows the white-leather department of a large chrome-calf tannery.

White Elk Side Leather

Finish No. 19 (Röhm & Haas): Mix 75 parts of Primal F-31, 25 parts of Primal F-32, 50 parts of Primal White and 75 parts of water.

Finish No. 20 (Röhm & Haas): Mix 10 parts of Orthochrom Intensive White, 24 parts of Binder 114-2, 2 parts of Binder 114-1 and 50 parts of Thinner 395.

Finish No. 21 (Röhm & Haas): Mix 70 parts of Orthoclear Top Finish D, 10 parts of Etonal White D, 50 parts of Dull Finish D and 200 parts of Thinner D.

If two coats of the same finish are applied, the second is given with strokes at right angles to the strokes of the first coat. Swab onto the leather two coats of Finish No. 19 and dry. Then spray on two coats of Finish No. 20 and dry. Smooth plate at 150° F. and board three ways. Then spray on one coat of Finish No. 21, dry and the finishing is completed.

White Sheep Pouch Bag Leather

Finish No. 22 (Röhm & Haas): Mix 50 parts of Primal F-31, 50 parts of Primal F-32, 150 parts of Primal White and 200 parts of water.

Finish No. 23 (Röhm & Haas): Mix 10 parts of Orthochrom Intensive White, 25 parts of Binder 114-2, 5 parts of Dull Finish No. 15 and 30 parts of Thinner 325.

Spray on two coats of Finish No. 22 and dry. Then spray on two coats of Finish No. 23. If the leather is to be embossed, spray on one more coat of Finish No. 23 after embossing.

This makes also an excellent method for finishing white basketball leather.

Glazed Kid Leather

Finish No. 24 (Hauthaway): Mix 4 parts of Kidco, 2 parts of No. T1281 Binder and Top Coat, 2 parts of No. T251 and 2 parts of water.

Apply 1 coat of Finish No. 24 by hand, dry, glaze and stake. Apply a second coat by hand, dry, glaze and stake. Spray on a third coat, dry, glaze and stake. Then apply a top coat made by mixing 1 part of egg albumin or blood albumin with 1 part of milk and water as needed to get the best results. Dry, glaze and stake.

Fig. 388 shows a group of operators finishing goatskins by hand and Fig. 389 shows hand grainers boarding finished goatskins.

Lining Kid Leather

Finish No. 25 (Röhm & Haas): Mix 100 parts of Primal F-32, 100 parts of Primal Color and 200 parts of water.

Finish No. 26 (Röhm & Haas): Mix 2 parts of Glazing Finish G-1, 1 part of Glazing Finish GS, 1 part of Orthochrom Intensive Gloss White and 6½ parts of Thinner 345.

Swab on two coats of Finish No. 25, dry and smooth plate. Then spray on one coat of Finish No. 26, glaze, stake and iron.

Crushed Kid Leather

Finish No. 27 (Röhm & Haas): Mix 10 parts of Primal F-32, 10 parts of Primal F-31 and 15 parts of water.

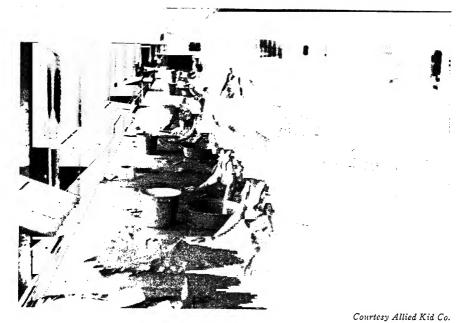


Fig. 388. Finishing Goatskins by Hand.

Fig. 389. Boarding, or Hand Graining, Chrome-tanned Goatskins.

Finish No. 28 (Röhm & Haas): Mix 1 part of Orthochrom Intensive Color, 5 parts of Binder 114-2, 3 parts of Glazing Finish G-1, 2 parts of Dull Finish No. 15 and 20 parts of Thinner 325.

Swab on two coats of Finish No. 27, dry and then spray the flesh side with water. Then board three ways and dry. Then spray with one coat of Finish No. 28, dry and board three ways again. Then rub up the tips.

Sheepskin Garment Leather

Finish No. 29 (Röhm & Haas): Mix 6 parts of Primal F-32, 6 parts of Primal Color and 12 parts of water.

Finish No. 30 (Röhm & Haas): Mix 10 parts of Orthoclear Top Finish D,

1½ parts of Intensive Colors and 20 parts of Thinner D.

Finish No. 31 (Röhm & Haas): Mix 16 parts of Orthochrom Intensive Colors, 3 parts of Binder 811-1, 37 parts of Glazing Finish G-1, 20 parts of Dull Finish No. 137, 20 parts of Dull Finish No. 2 and 300 parts of Thinner 335-A.

For the poorer grades of skins, swab on two coats of Finish No. 29, dry and spray on one coat of Finish No. 30. Then polish, iron and plate.

For first-class skins, spray on two coats of Finish No. 31, dry, polish and iron.

Sheep Lining Leather

Finish No. 32 (Röhm & Haas): Mix 75 parts of Primal F-31, 25 parts of Primal F-32, 100 parts of Primal Color and 200 parts of water.

Finish No. 33 (Röhm & Haas): Mix 8 parts of Orthochrom Intensive Colors, 8 parts of Binder 811-1, 100 parts of Glazing Finish G-1 and 150 parts of Thinner 325.

Spray on one heavy coat of Finish No. 32, dry and smooth plate cold. Then spray on one heavy coat of Finish No. 33, dry, glaze and plate.

Hat Sweat-band Leather

Finish No. 34 (Hauthaway): Mix 1 part of Special Finish, 1 part of No. T1281 Binder and Top Coat and 1 part of water.

Finish No. 35 (Hauthaway): Mix 5 parts of No. T1281 Binder and Top Coat, 1 part of No. 7800A Binder and Top Coat and 6 parts of water.

Apply two coats of Finish No. 34 by hand, dry, stake and roll. Then apply one coat of Finish No. 35 and dry.

Unglazed Wax Enamel Leather

Finish No. 36 (Hauthaway): Mix 4 parts of Wax Enamel, 2 parts of No. T1281 Binder and Top Coat, ½ part of No. 235 Dribrite Binder and Top Coat and 6 parts of water.

Finish No. 37 (Hauthaway): Mix 4 parts of Wax Enamel, 6 parts of No. T1281 Binder and Top Coat, 1½ parts of No. 235 Dribrite Binder and Top Coat and 14 parts of water.

Finish No. 38 (Hauthaway): Mix 1 part of No. 235 Dribrite Binder and Top Coat, 6 parts of No. T1281 Binder and Top Coat and 7 parts of water.

Apply one coat of Finish No. 36 and dry. Apply one coat of Finish No. 37, dry, stake and roll. Apply one coat of Finish No. 38 and dry.

Colored Side Leather

Finish No. 39 (Quinn): Mix 24 oz. of RV Pigment, 12 oz. of Dye Solution, 12 oz. of water, 2½ oz. of 100 Binder, 4 oz. of BG 9325 Binder and 1 oz. of aqua ammonia.

Finish No. 40 (Quinn): Mix 10 oz. of RV Pigment, 5 oz. of BG 9325 Binder, 20 oz. of water and $\frac{1}{2}$ oz. of formaldehyde.

Finish No. 41 (Quinn): Mix 4 oz. of T 5478 Top Finish, 8 oz. of water, $\frac{1}{2}$ oz. of RV Pigment, and $\frac{1}{16}$ oz. of formaldehyde.

Finish No. 42 (Quinn): Mix 7 oz. of T 5478 Top Finish, 10 oz. of water and $\frac{1}{16}$ oz. of formaldehyde.

Apply one coat of Finish No. 39 and dry. Apply one coat of Finish No. 40, dry and plate at 170° F. Apply one coat of Finish No. 40, dry and plate at 160° F. Apply one coat of Finish No. 41 and dry. Apply one coat of Finish No. 42, dry and plate at 125° F.

Gun-metal Side Leather

Finish No. 43 (Hauthaway): Mix 2 qts. of No. T 9561 Black Finish, 1 qt. of Nigrosine-J solution (1 lb. per gal.), 1 qt. of water and 2 oz. of rubber latex.

Finish No. 44 (Hauthaway): Mix 2 qts. of No. T 9561 Black Finish, 1 qt. of Nigrosine-J solution (1 lb. per gal.), 1 qt. of No. T 1281 Binder and Top Coat and 1 qt. of water.

Finish No. 45 (Hauthaway): Mix 2 qts. of No. T 9561 Black Finish, 1 qt. of Nigrosine-J solution (1 lb. per gal.), 2 qts. of No. T 1281 Binder and Top Coat and 2 qts. of water.

Finish No. 46 (Hauthaway): Mix 1 part of No. 150 Black Top Coat with 2 parts of water.

Apply one coat of Finish No. 43 and dry. Apply one coat of Finish No. 44 and dry. Apply one coat of Finish No. 45 and dry. Apply one coat of Finish No. 46, dry and plate. Apply one coat of Finish No. 46, dry and plate.

Water-lacquered Leathers

Finish No. 47 (Kepec): Mix 1 part of Emullo with 1 part of water. Emullo is a water emulsion of lacquer.

Swab on one coat of Finish No. 47 and dry. Then spray on one coat of Finish No. 47 and dry. If desired, apply one coat of a mixture of 1 part of Watersoluble Finish No. 91 and 2 parts of water.

Elk Side Leather

Finish No. 48 (Hauthaway): Mix 4 qts. of Special Finish, 3 qts. of No. T 1281 Binder and Top Coat, 1 qt. of No. T 1122 Binder and Top Coat, 4 qts. of water and 9 oz. of rubber latex.

Finish No. 49 (Hauthaway): Mix 4 qts. of Special Finish, 3 qts. of No. T 1281 Binder and Top Coat, 1 qt. of No. T 1122 Binder and Top Coat and 4 qts. of water.

Apply one coat of Finish No. 48 and dry. Apply one coat of Finish No. 49 and dry. If a brighter finish is desired add to these finishes some No. 235 Dribrite Top Coat and Binder. If a softer finish is desired, add some No. 7800 A Top Coat and Binder.

Lining Splits

Finish No. 50 (Röhm & Haas): Mix 100 parts of Primal A, 30 parts of Primal Color and 30 parts of water.

Finish No. 51 (Röhm & Haas): Mix 10 parts of Orthochrom Intensive Color, 5 parts of Binder 114-1, 40 parts of Binder 114-2 and 75 parts of Thinner 325.

Brush on two coats of Finish No. 50 and level off with plush swab. Roll while

still damp. Spray with one coat of Finish No. 51, dry and emboss at 180° F. If desired, spray on one coat of Finish No. 51 after embossing.

Horsehide Garment Leather

Finish No. 52 (Röhm & Haas): Mix 25 parts of Primal F-31, 25 parts of Primal F-32, 35 parts of Primal Color, 150 parts of water and ½ part of aqua ammonia.

Finish No. 53 (Röhm & Haas): Mix 10 parts of Orthoclear Top Finish D, 2 part of Orthochrom Intensive Colors, 2 parts of Dull Finish DS, and 30 parts of Thinner D.

Swab on two coats of Finish No. 52, dry and stake. Spray on one coat of Finish No. 53, dry and plate lightly at 120° F.

Case Leather

Lacquer Method: Finish No. 54 (Röhm & Haas): Mix 5 parts of Orthochrom Intensive Color, 20 parts of Binder 114-1, 10 parts of Binder 114-2 and 45 parts of Thinner 325.

Finish No. 55 (Röhm & Haas): Mix 10 parts of Lustrone Colors, 10 parts of Glazing Finish GS, 20 parts of Glazing Finish G-1 and 70 parts of Thinner 325.

Smooth plate and spray on Finish No. 54 until an even color is obtained which hides stains. Then spray on two or three coats of Finish No. 55.

Primal Method: Finish No. 56 (Röhm & Haas): Mix 100 parts of Primal A, 50 parts of Primal Color and 150 parts of water.

Finish No. 57 (Röhm & Haas): Mix 10 parts of Orthochrom Intensive Colors, 30 parts of Binder 114-2 and 50 parts of Thinner 325.

Finish No. 58 (Röhm & Haas): Mix 15 parts of Lustrone Colors, 20 parts of Glazing Finish GS, 80 parts of Glazing Finish G-1 and 200 parts of Thinner 325.

Swab on two coats of Finish No. 56 and roll while damp. Dry and spray on two coats of Finish No. 57, dry and smooth plate at 180° F. Spray on two coats of Finish No. 58. Smooth plate or glaze.

The fatliquoring, dyeing and finishing of aniline bag and case leathers have already been described in Chapter 15, p. 485.

Black Vegetable-tanned Strap and Portfolio Leathers

Finish No. 59 (Hauthaway): Mix 1 part of No. 4020 Black Finish, 1 part of No. 4021 Binder and Top Coat, 1 part of Black Kafco, 1 part of flaxseed solution and 1 part of water.

Finish No. 60 (Hauthaway): Mix 2 parts of No. 4021 Binder and Top Coat, 1 part of flaxseed solution and 3 parts of water.

Apply one coat of Finish No. 59, dry, brush and roll. Apply second coat of Finish No. 59, dry, brush and roll. Apply one coat of Finish No. 60, dry, brush and roll.

Upholstery Leather (handbuff)

Finish No. 61 (Röhm & Haas): Mix 18 parts of Primal Color, 15 parts of Primal C, 4 parts of sulfonated castor oil, 2 parts of aqua ammonia, 100 parts of Primal F-31 and 45 parts of water.

Finish No. 62 (Röhm & Haas): Mix 10 parts of Orthochrom Intensive Colors, 4 parts of Binder 114-1, 26 parts of Binder 114-2 and 40 parts of Thinner 325.

Finish No. 63 (Röhm & Haas): Mix 90 parts of Orthoclear Finish K, 10 parts of Dull Finish No. 15 and 150 parts of Thinner 325.

Swab on two coats of Finish No. 61 and dry. Spray on two coats of Finish No. 62, dry and emboss at 180° F. Board with grain side out and then spray on two coats of Finish No. 63 and dry.

Vegetable-tanned Football-helmet Leather

Finish No. 64 (Röhm & Haas): Mix 1 part of Binder 114-1 with 2 parts of Thinner 335-A.

Finish No. 65 (Röhm & Haas): Mix 2 parts of Binder 114-1, 1 part of Binder 114-2 and 4 parts of Thinner 335-A.

Finish No. 66 (Röhm & Haas): Mix 1 part of Orthochrom Intensive Colors, 5 parts of Binder 114-2 and 10 parts of Thinner 355.

Swab on two coats of Finish No. 64, dry and smooth plate at 160° F. Spray on one coat of Finish No. 65, dry and spray on one coat of Finish No. 66. Emboss or smooth plate at 160° F. Then spray on one coat of Finish No. 66.

Baseball Leather

Finish No. 67: Mix 9 fl. oz. of Finish No. 1, 5 fl. oz. of Finish No. 3, 3 fl. oz. of ox blood, 2 fl. oz. of diethylene glycol and 1 fl. oz. of a solution of 8 oz. sulfonated linseed oil per gal.

Finish No. 68: Mix 2 fl. oz. of Finish No. 3, 9 fl. oz. of ox blood, 9 fl. oz. of fusel oil and 9 fl. oz. of glycerin.

Finish No. 69: Mix 7 fl. oz. of Finish No. 3, 24 fl. oz. of ox blood, 3 fl. oz. of diethylene glycol and 6 fl. oz. of a solution containing 8 oz. of sulfonated linseed oil per gal.

Swab on one coat of Finish No. 67, dry, glaze under high pressure, stake and iron. Swab on one coat of Finish No. 68 and dry. Swab on one coat of Finish No. 69, glaze under low pressure, stake and iron.

Two-tone Basketball Leather

Finish No. 70 (Röhm & Haas): Mix 50 parts of Primal F-31, 50 parts of Primal F-32, 50 parts of Primal Color, and 100 parts of water.

Finish No. 71 (Röhm & Haas): Mix 10 parts of Orthochrom Intensive Colors, 25 parts of Binder 114-2, 5 parts of Dull Finish No. 15 and 50 parts of Thinner 325.

Finish No. 72: Mix 1 lb. of Finish No. 4x with 1 gal. of Finish No. 1.

Select the colors of Finishes No. 70 and No. 71 so that they will impart the colors desired on the raised portions of the embossed leather. Select the colored pigments of Finish No. 72 so that they will impart the colored desired on the depressed portions of the embossed leather.

Spray on two coats of Finish No. 70 and dry. Then spray on two coats of Finish No. 71 and dry. Then swab on enough of Finish No. 72 to cover the entire leather with its color and dry. Then emboss at 160° F. under heavy pressure. Then roll cheese-cloth into a ball and dampen it slightly with ammonia water, wringing out any excess, and wipe the casein-pigment finish off from the high spots in the leather to get the two-tone effect desired. When the desired appearance has been obtained, spray on one coat of Finish No. 71 made up without the addition of any color.

Golf-grip Leather

Finish No. 73 (tacky finish): Mix by weight 100 parts of Blendoyl (The Pierce Oil Products Corp., East Rochester, N. Y.), 50 parts of beeswax and 50



Fig. 390. Leaf-laying Rooms Where Gold and Silver Leathers Are Made.



Fig. 391. Applying Gold and Aluminum Leaves to Leather.

parts colophony (common rosin). Heat the mixture at 212° F. for 20 minutes and stir into it 300 parts of naphtha of 0.74 specific gravity. Heat a mixture of 90 parts of light paraffin oil and 9 parts of aluminum stearate, mix until uniform and stir it into the above mixture. Continue to heat and stir until the mixture will not solidify upon cooling.

Apply to grain and flesh in such quantities that it completely penetrates the leather. The mixture can be diluted with naphtha and the leather dipped in it for 15 minutes, if preferred. After treating, hang the leather to dry until free from naphtha.

Saddle Leather

Saddle leathers, pigskins and any other fine vegetable-tanned leathers can be finished exactly as for vegetable-tanned calfskins with very satisfactory results. It is believed that enough has been given above to enable an experienced finisher, capable of making adjustments, to arrive at methods for finishing practically any kind of leather. Because of variations in many characteristics of leathers, a finisher must be able to make proper adjustments in very many cases.

Gold and Silver Leathers

Leathers finished with pure gold or aluminum are much in demand for formal wear and the writer is indebted to Dr. Henry Rose, of Allied Kid Co., for the following information concerning this interesting finishing operation. The gold leathers are coated with pure gold leaf, but the silver leathers are now coated with aluminum leaf. The gold leaf has a thickness of from 1/25,000 to 1/30,000 inch and is pure 23-carat gold. Just a little silver or copper in the gold changes its color. The aluminum leaf is only 1/50,000 inch in thickness and consists of 99.4 percent pure aluminum. Impurities in the aluminum tend to make it brittle.

After proper retanning, the skins are glued onto boards. This retanning varies according to the skins and almost any kind of skin could be properly prepared for gold and silver. Fig. 390 shows a part of the leaf-laying rooms, and Fig. 391 shows the leaves ready to be applied.

After the skin has dried on the board, a glue, consisting of potato starch, alone or mixed with gelatin, is rubbed into the skin. Two or more coats may be applied, drying after each coat. Finally, a solution of from 10 to 20 grams of gelatin per gallon is applied by means of a camel-hair brush. The leaves are picked up with a screen frame and gently placed on the wet surface of leather. After drying over night, the leaves should adhere tightly to the skin. A few years ago, Dr. Rose received a patent on a frame for picking up leaves. Fig. 392 shows the transfer of the leaves from the screen to the skin. By touching the screen lightly with the fingers, the leaves are released from the screen and pass onto the skin. After drying, the aluminum overlaps are merely wiped off, but the gold overlaps are removed with a vacuum cleaner to save the gold. After the skin is thoroughly dried and the adhesion of the metal leaves is satisfactory, the silver skins are plated, but the gold skins are glazed. Fig. 393 shows the glazing operation on gold-coated leather.

Patent Leathers

The name *patent* as applied to patent leathers is a misnomer, because the process of making patent leather is not patented, but evolved through the years. It is a name applied to leathers finished with linseed-oil varnish. The leather is sometimes called either japanned leather or enameled leather. It is usually chrome tanned.



Ftg. 392. Showing Transfer of Gold and Aluminum Leaves from Screen to Skin Surfaces.

If the leather contains greases that might interfere with the varnish, it is usually degreased with naphtha before varnishing. The leather is buffed only if necessary to remove grain defects. Usually three coats of varnish are applied, which differ in composition.

The First Coat. In one process, the first coat, or *daub*, is made by pouring 50 gals. of linseed oil into a 100-gal. cast-iron kettle, with a rounded bottom and diameter of about 4 ft., and adding about 50 oz. of raw umber as a *drier*. The mixture is heated at such a rate that its temperature rises to about 560° F. in the course of two hours. This temperature is maintained and the mixture is ladled continuously. The ladle is a small copper bucket attached to an iron handle about 8 ft. long.

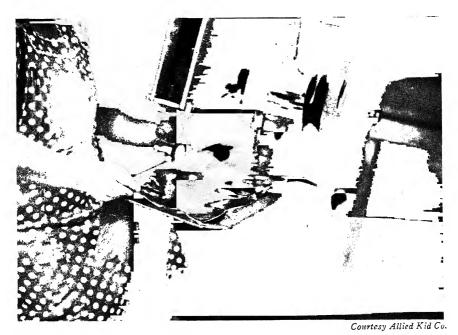


Fig. 393. Glazing Leather Coated with Pure Gold.

After several hours the oil dripping from the ladle when inverted forms large leaves, whose character indicates the consistency of the daub. The ladle is finally replaced by a fork having a bar extending over the points of the prongs to hold them rigidly in place. There are 5 prongs about 12 inches long and spaced about 2 inches apart. The kettle is removed from the flame and "puddled" with the fork until the daub breaks and lies on the fork, which usually occurs when the temperature has dropped to about 489° F. The outside of the kettle is then sprayed with water until the temperature has dropped to about 409° F. Then 75 gals. of naphtha is added, with continuous puddling, and the mixture is allowed to cool, after which it is stored in covered tanks until used. Aging is neither necessary nor desirable.

The practical men of the trade generally regard their methods for boiling the oil as trade secrets, which they guard jealously. The real secret consists in

the ability to recognize when the oil has been boiled long enough to permit adding the naphtha. Normal variations in raw linseed oil make it impossible to set the time, temperature, and mechanical stirring definitely. Each batch of oil requires variations in these factors to take care of variations in composition of the oil. The master japanner knows when to stop the boiling by observing the changing consistency of the oil, the way it drips from the ladle, the way it strings when squeezed between the palms of the hands and then drawn out, and the way it feels when rubbed between fingers and thumb. Some japanners wisely keep on hand



Fig. 394. Vertical Section of Patent Side Leather.

Location: butt.

Thickness of section: 30 microns, or 0.00118 inch.

Magnification: 75 diameters.

for comparison samples of other batches that have proved satisfactory on leather. The chemist has now introduced viscosity measurements in order to follow the progress of the boiling of the oil, but the end-point is still determined, in most tanneries, by the observations of the master japanner.

Before the daub is applied to leather, it is thinned further with naphtha and coloring matter is added. Where pigments are added, the mixture is ground in a mill, frequently a ball mill, in order to get as intimate and fine a mixture as possible. The most common finishes are black and may be made by using carbon black and Prussian blue. These can be incorporated satisfactorily by heating to about 149° F. and stirring.

The skins to be finished are placed in open toggle frames. The toggles are small spring clamps to which long cords are attached. The jaws of the toggle grip the leather firmly. The toggles are placed along the perimeter of the skin, a few inches apart. The strings are then drawn tightly and caught in cleats nailed onto the frames. The skin is drawn out so that it lies flat and tight like the skin on a drum.

The daub, having the consistency of a soft putty, is smeared over the grain surface of the leather and rubbed out smooth with a dull, steel blade, called a



Fig. 395. Vertical Section of Patent Kid Leather.

Location: butt.

Thickness of section: 30 microns, or 0.00118 inch.

Magnification: 75 diameters.

slicker. The daub can be thinned out further with naphtha and applied with a sponge and then rubbed into the leather with the palms of the hands. The amount of material applied is such as to give a dried coat about 0.0025 inch thick. The frames are packed together in an upright position on trucks and wheeled into a drying chamber where the temperature is kept at about 104° F. Next day the skins are ready to receive the second coat.

The Second Coat. The second coat is usually called the *brush coat*. It is made by pouring 50 gals. of linseed oil into the iron kettle and adding from 50 to 150 oz. of raw umber and 6 to 36 oz. of litharge (lead oxide), according to tests

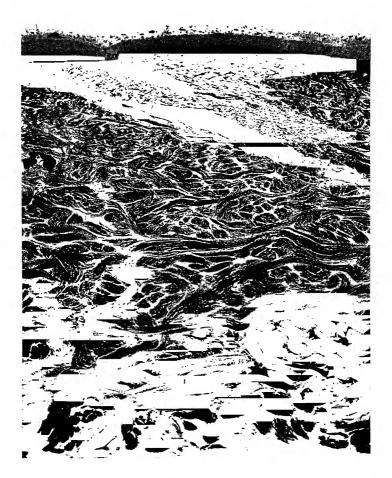


Fig. 396. Vertical Section of Patent Colt Leather.

Location: shoulder.

Thickness of section: 30 microns, or 0.00118 inch.

Magnification: 75 diameters.

on the raw oil. In the course of two hours, the temperature of the mixture is raised gradually to about 560° F. and it is maintained there for from 3 to 4 hours, during which time the oil is ladled continuously. When strings up to 2 inches in length form on the lip of the inverted ladle, heating is stopped, but the ladling is continued vigorously until leaves, which break more or less sharply, form on the inverted ladle. When this occurs, the temperature has usually dropped to about 356° F. Then 50 gals of naphtha is added and the mixture is cooled and placed in storage tanks until used.

This material is thinned with naphtha to a good flowing consistency and applied to the dried first coat with a camel-hair brush about 8 inches wide. The frames containing the leather with brush coat applied are then kept in drying ovens

at from 131° to 140° F. for from 16 to 24 hours. The dried second coat also has an average thickness of about 0.0025 inch.

The Third Coat. The third coat is usually called the varnish coat. It is made by pouring 50 gals. of linseed oil into the iron kettle and adding 200 oz. of Prussian blue and 4 to 10 oz. of litharge. In the course of two hours, the temperature is gradually raised to about 532° F. and it is maintained there for about three hours, during which time the oil is ladled continuously. Samples are withdrawn at intervals and examined by working them between the fingers; comparisons are made with previous samples known to be satisfactory. When the oil has been boiled long enough, the heating is stopped and it is cooled and thinned with 37½ gals. of naphtha. It is then placed in storage tanks and kept at least three weeks before using to allow it to clear.

Before applying the varnish coat, the leather is carefully inspected for dust particles or lumps on its surface. If necessary, the surface is smoothed by rubbing with a pumice stone, as is done with any other surface to smooth it to receive a fine varnish coat. The varnish is applied by highly skilled workmen, who give it a smooth and even surface. The frames containing the leather are then rolled back into the ovens and kept at a temperature of from 140 to 150° F. for from 12 to 16 hours. The dried top coat may have an average thickness of about 0.005 inch, or about the thicknesses of both first and second coats combined.

Sunning. After this last drying, the finished surface of the leather still feels sticky, but this is overcome by subjecting the varnished surface to the action of sunlight. The ultraviolet rays of the sun produce certain chemical changes in the varnish that eliminate stickiness. It was a common sight around patentleather tanneries to see hundreds of frames of patent leather in the yard exposed to sunlight. In bright sunlight about 5 hours is sufficient to bring about the desired effect. Many tanners now use ultraviolet lamps to get the same effect. After sunning, the leather is ready for delivery.

Lacquering. Some tanners shorten the process by the use of lacquers over the daub coat or over the second coat, but many still prefer the pure linseedoil varnishes.

Photomicrographs. Fig. 394 shows a cross-section of patent cow side leather in which the three coats of varnish can be seen very distinctly. Fig. 395 shows a cross-section of patent leather made from goatskins, and Fig. 396 shows one of the popular patent horsehide. All three are chrome tanned.

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Chapter 18

Sole and Heavy Leathers

The making of vegetable-tanned sole leather will now be described for the operations which follow those described in Chapter 11. The leather coming from the layers or from the tanning drums is fully tanned, but requires a number of subsequent operations before it becomes commercial sole leather. Because these operations differ so greatly from those for vegetable-tanned light leathers, it was considered desirable to give separate descriptions of them to avoid confusion.

Cropping

If the leather coming either from the layer vats or the tanning drums has not already been cut into sides, this is done first. Then each side is *cropped*; that is, the belly is cut off. Fig. 397 shows the divisions into which a side of sole leather may be cut by the tanner. The side is exactly one-half of the whole hide

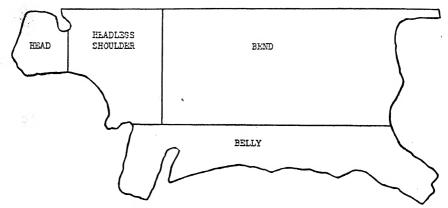


Fig. 397. Divisions into Which a Side of Sole Leather is Cut.

Crop consists of bend, headless shoulder and head.

Back consists of bend and headless shoulder.

cut along the line of the backbone. The belly is usually cut off, from the layers, so that its weight is approximately 23 percent of that of the side. What is left, after the belly has been cut off, is called a crop. At some later stage in the process, the tanner may find it convenient to cut the crop into shoulder and bend. The shoulder may be cut further into head and headless shoulder. Only the approximate relative dimensions of these parts can be shown, because hides vary in the relative values of their parts and a tanner specializing in the highest grade of bends may cut his bends to a smaller relative area. Sometimes shoulders are cut with the heads left on. In very few cases, a tanner may cut the whole hide into two bellies, one double bend and one double shoulder. As the bend contains the

choicest leather and the belly the poorest, it is frequently advisable to carry on the operations from the layers with the various parts separated. Most tanners simply divide into bellies and crops at this stage. The bellies do not have a sufficient value to warrant all the operations to which the crops are subjected. Some tanners also cut off the heads at this stage. A crop with head removed is called a back.

After cropping, the crops are soaked for about 30 min. in a liquor of about 10° barkometer at 100° F. This leaches some of the stronger liquor from the outer layers of the crops before they are wrung. This *rinse* liquor is used for successive lots until its barkometer reading is raised to about 15°. Then enough of it is run to the leach house so that the remaining liquor made up with water has a barkometer reading again of 10°. Bellies are usually left in the rinse liquor over night. After rinsing, crops, backs and bends are usually *extracted*. Bellies are not usually extracted.



Fig. 398. Loading Sole-leather Crops into Extract Drum.

Extracting

Before extracting, the stock is put through a Quirin wringer to reduce its water content; it is then put into a drum 9 ft. in diameter by about 8 ft. wide and running at about 18 r.p.m. An average pack is the equivalent in weight of about 80 crops. The composition of the extract liquor varies in different tanneries, but may consist of a liquor of about 25° Baumé containing one third of cutch and two-thirds of quebracho on tannin basis, or about 38 percent tannin, bisulfited

together. It is really a highly concentrated liquid extract; in fact, it is made as strong as possible in liquid form. To it is added about 2 percent of its weight of sulfonated cod oil. For each 100 lbs. of wrung weight of stock in the drum, about 15 lbs. of this mixture is taken and heated to 150° F. The drum is started running and the mixture is run onto the stock through the hollow gudgeon of the drum. After about 90 min., the extract is almost completely absorbed, and the stock is then hauled out. Because of variations in water content of the wrung stock, precise quantities per unit weight cannot be given, but for the conditions obtaining in any one tannery, it is easy to work out a set of rules as determined by the results obtained.

Fig. 398 shows a workman loading sole-leather crops into an extract drum from the floor above and Fig. 399 shows the pack being dumped after extracting and being piled on a truck on the floor below.



Courtesy Endicott-Johnson Corp.

Fig. 399. Piling Sole-leather Crops after Extracting.

Tempering

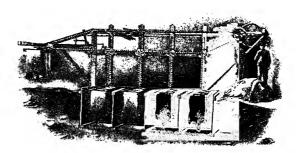
The object of extracting is to increase the load held by the leather and to increase the ultimate yield of finished leather. To do this quickly, very concentrated extracts are used. As it is not desirable to have the leather go forward containing too much uncombined tannin, the latter is reduced somewhat by the operation of tempering. There are enough tempering vats to take care of a week's production of crops. Each tempering vat is about 9 ft. by 9 ft. by about 6 ft. deep and contains tan liquor of about 45° barkometer reading. About 300 crops from

the extract drum are put into each vat and allowed to remain there for a week. During this time, some extract is leached out of the leather and the barkometer reading rises from about 45° to 50°. The crops are then taken out and enough liquor is run to the leach house so that the remaining liquor, when made up to volume with water, has a barkometer reading of 45°. The crops are then rinsed again for 30 min. in liquor of about 10° barkometer, exactly as before extracting, and they are then ready for bleaching.

Bellies are not extracted and so are not tempered. After cropping, they are rinsed and sent directly to the bleach.

Bleaching

The principle of bleaching sole leather is exactly the same as that of bleaching vegetable-tanned calf leather described in Chapter 14; but sole leather does not lend itself readily to the drum operations and so it is done in still vats. These vats are conveniently arranged in series of 4 vats each; a suitable size for each vat is 7 ft. by 6 ft. by 6 ft. deep. Each vat is equipped with a movable rack. Each rack is fitted to hold 14 sticks, each 7 ft. long, spaced about 4½ inches apart. Two crops can be hung over each stick so that both head and tail hang downward.



Courtesy Turner Tanning Machinery Co. Fig. 400. Bleaching Machine.

The first vat contains pure water at a temperature of 125° F. The second vat is filled with water at 125° F. and 100 lbs. of soda ash is dissolved in it. The third vat is filled with water and 250 lbs. of 66° Baumé sulfuric acid is dissolved in it. The fourth vat contains only pure water at 100° F. The workmen should be cautioned that higher temperatures may cause irreparable damage.

Above the vats, a mechanical device is erected for raising the racks loaded with leather and moving them from one vat to the next in the series. A rack of leather is moved through all four vats, remaining for about 5 min. in each. As a rule, all four racks move together, so that a rack of new leather enters the first vat each time that one leaves the fourth vat. During the time that the four racks of leather are submerged in liquor, a new rack is being loaded with leather to enter the first vat, the leather is being removed from the rack that has just left the fourth vat, and the workmen are weighing off the soda ash and sulfuric acid for strengthening the second and third vats, respectively.

Fig. 400 shows the Turner bleaching machine, which consists essentially of the mechanical device for moving the racks from one vat to another. Upon

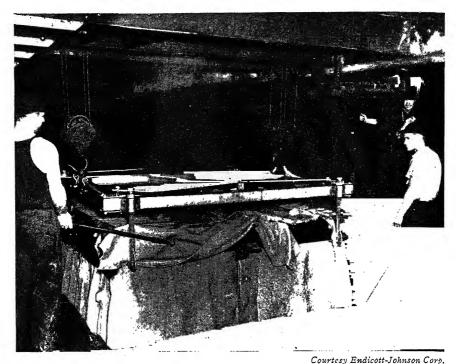


Fig. 401. Mechanical Movement of Sole-leather Crops in Bleaching.

leaving the fourth vat, the crops are automatically dumped onto a platform and the rack returns to be loaded again before entering the first vat. Various tanneries have different arrangements for accomplishing the same result. Fig. 401 shows a rack of crops coming out of a bleaching vat in a large, modern sole-leather tannery.

Since each vat is used for a number of successive racks of leather before making up fresh, it is necessary to strengthen the second and third vats after each rack has passed through it. In routine operation for the size of vat and number of crops per rack described above, a tanner may add 4 lbs. of soda ash to the second vat and 8 lbs. of sulfuric acid to the third vat for each rack that has passed through. However, it is much safer to have periodic analyses made by a chemist to determine how much of each material must be added per rack to maintain the original concentrations of soda ash and sulfuric acid. These analyses consist only of simple titrations that can be made in very few minutes.

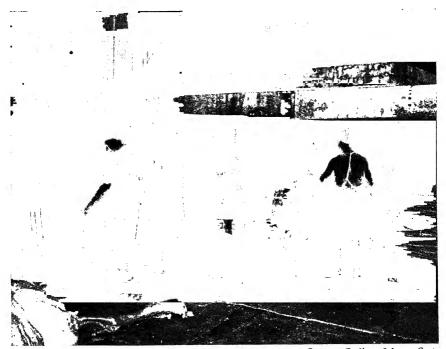
The size of rack described will hold 28 crops or 70 bellies, since the bellies can be hung 5 to the stick.

After bleaching, the crops are again wrung out to remove the bulk of the water before they enter the *oil wheel*. Fig. 402 shows the operation of wringing sole-leather crops. The same operation is performed both before extracting and before running in the oil wheel.

Bellies are also wrung out and sent to the oil wheel, but the treatment in the oil wheel may be very different.

The Oil Wheel

The oil wheel may be a drum 8 ft. in diameter and 9 ft. wide, running at 20 r.p.m., but this varies greatly in different tanneries. The object of oil-wheeling is to incorporate materials into the leather that will increase the ultimate yield and improve the properties of the finished leather. Finders' leather is a name given to the hard and firm leather preferred by cobblers for repairing shoes. Manufacturers' leather is the name applied to sole leather sold directly to shoe manufacturers, which is usually softer and mellower than finders' leather. Flexible sole leather is softer and more flexible than manufacturers' leather and is used to make comfort shoes; incidentally, flexible leather will greatly outwear the firmer leathers. Any variations in the operations following bleaching greatly influence the characteristics of the finished leather and some tanners have gained reputations for making leathers of certain specific properties particularly well. For this reason, the operations in different tanneries may differ greatly in details, although the general operations in nearly all tanneries are essentially the same.



Courtesy Endicott-Johnson Corp.

Fig. 402. Wringing Sole-leather Crops for Extracting or for Oil-wheeling.

One of many procedures for oil-wheeling crops is as follows: Put 3000 lbs. wrung weight of stock into the dry drum. Mix dry 24 lbs. of goulac (Am. Gum Products Co.), 40 lbs. of Epsom salt, 10 lbs. of aluminum sulfate, 12 lbs. of powdered niter cake (sodium bisulfate), and 10 lbs. of colloidal clay-B (Saxe-Rushworth Co.), and add to drum. Start it running, and add through the hollow gudgeon of the drum a mixture of 80 lbs. of corn syrup, 24 lbs. of cod oil and

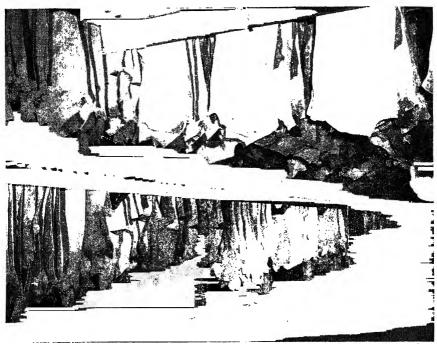
6 lbs. of sulfonated cod oil at 160° F. Run 40 min. and dump the pack. Note that no water is added to the drum. At the end of the 40 min., all the materials should be absorbed by the leather.

For an oil-wheel load of 200 bellies, use per 100 lbs. wrung weight 3 lbs. of goulac, 4 lbs. of Epsom salt, 2 lbs. of niter cake, 10 lbs. of corn syrup and 3

lbs. of cod oil. Run as for the crops.

After the stock comes from the oil wheel, the crops are hung in a damp room by the head, with tail hanging downward, for 24 hours to condition for setting. They are then set out under heavy pressure on a drum setting-out machine, like that shown in Fig. 256 of Chapter 14. They are then hung to dry.

The bellies are hung over sticks to condition for 24 hours and are then set out on a belly setting-out machine, like that shown in Fig. 295 of Chapter 15, after this they are hung to dry.



Courtesy Endicott-Johnson Corp.

Fig. 403. Sole-leather Crops Hanging in Drying Rooms.

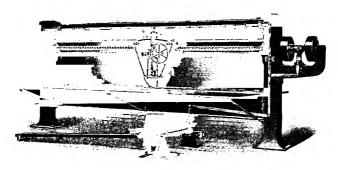
Drying

Both crops and bellies are hung over sticks, grain side out to dry. Sole-leather crops hanging to dry are shown in Fig. 403. To prevent serious darkening and discoloration of the leather, it is usually dried very slowly at relatively low temperatures. Sole leather at this stage contains a great deal of material that readily combines with oxygen from the air, forming resinous materials of very dark color, and the rate of oxidation increases very markedly with rise of temperature. In some tanneries, the temperature and humidity of the drying rooms are so controlled that the drying is never completed in less than 10 days.

After the stock is first hung to dry, the doors are closed so that there is practically no ventilation in the drying rooms. As the drying progresses, more and more ventilation is allowed; but the temperature is not raised above that of room temperature until after the stock has been hanging for at least 5 days, and then it is never raised above 90° F. until after the stock is fully dried.

The Sour Dip

The sour dip takes its name from the fact that it consists of a solution of Epsom salt and corn sugar, which is allowed to ferment and sour, with the formation of organic acids. The sour-dip liquor is made up in a large tank for fermentation. According to one method, 1200 lbs. of corn sugar, 720 lbs. of Epsom salt and 2 lbs. of yeast are dissolved in 1200 gals. of water at 100° F. and allowed to ferment until the pH value of the liquor drops to 3.0. This liquor is then diluted to a barkometer reading of 35° and is run into dipping boxes of convenient size at a temperature of about 110° F. Each crop or belly taken after drying is dipped into the liquor and left there to soak for 20 min. The sour dip keeps the color of the leather bright and tends to prevent discoloration of the leather by oxidation. After sour dipping, the stock is again hung to condition over night, is again set out as smoothly as possible and is again hung to dry slowly.



Courtesy Turner Tanning Machinery Co.

Fig. 404. Horizontal Sole Leather Roller.

Sponging and Rolling

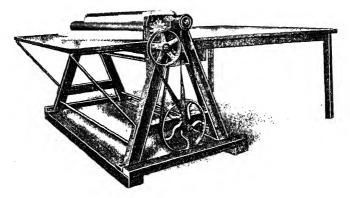
The dried crops are dipped one by one very quickly in a solution of 25 lbs. of Epsom salt and 2 lbs. of oxalic acid in 100 gals. of water and are piled down to condition for an hour. The grain surface of each is then washed with a sponging compound made as follows: To 70 lbs. of Nopcol (National Oil Products Co.) add 10 gals. of water and boil for 10 min. Then add 6 gals. of Nopcolene and 6 gals. of kerosene and continue to boil for 20 min. Dilute with water to make 100 gals. Wash the grain side of each crop with this mixture at a temperature of 150° F. This may be applied with a sponge, or more conveniently poured over the grain, using an automatic pump and hose, the excess liquor flowing back into a trough, from which the pumping is done. Hang to dry until the stock is in condition for rolling, which can be learned only by experience. Then roll the stock the first time.

The roller consists of a heavy roll, which passes over the grain side of the leather under very heavy pressure. Fig. 404 shows a Turner Roller sometimes used for this purpose. The roll is made of brass, 20 inches in diameter by 6 inches wide.

After the first rolling, the stock is hung to condition for about 2 or 3 hours and it is then rolled again. Sometimes it is sponged again between rollings. After the second rolling, the stock is again hung to dry completely.

Finishing

Apply a coat of Finish No. 13 (Chapter 17), with or without pigment as desired, dry and then roll again. After rolling, brush to desired luster on a brushing machine like that shown in Fig. 405. After brushing, the stock is ready for delivery.



Courtesy Turner Tanning Machinery Co.

Fig. 405. Sole Leather Brushing and Finishing Machine.

Finders' Bends

Leather for the very heavy and plump finders' bends is selected during the cropping operation and split into bends, shoulders and bellies. Since the operations are in general like those for crops, only the essential points of difference will be described.

After cropping, the bends are rinsed, wrung, extracted and tempered, but the time in the tempering vats is extended to 10 days because these bends are heavier than the crops. The bends are then rinsed and bleached. After bleaching, oil-wheeling and drying, the bends are dry-dipped, and are bleached and oil-wheeled a second time. In bleaching, each rack contains either 44 bends or 44 shoulders. In the first bleaching and oil-wheeling, the quantities of materials used are the same as for crops; but in the second bleaching only one-half of the quantities are used, and in the second oil-wheeling the same amount of corn syrup is used, but the quantities of other materials are cut in half.

The Dry Dip

After the bends have been bleached, oil-wheeled and dried the first time, they are dry-dipped. The dry-dip liquor consists of a mixture of one-third cutch extract and two-thirds quebracho extract on tannin basis, bisulfited together, and diluted to a barkometer reading of 55°. It is heated to 120° F. and the dry bends are

immersed in it and allowed to soak in it for an hour. The bends are then piled on a truck for an hour and are then given the second bleaching and the second oil-wheeling. They are again set out and dried slowly, after which the operations are the same as for crops. Shoulders are treated like crops all the way through. A vertical section of a finders' bend is shown in Fig. 406.



Fig. 406. Vertical Section of Vegetable-tanned Sole Leather (Finders' Bend).

Location: butt.

Thickness of section: 40 microns, or 0.00157 inch.

Magnification: 23 diameters.

Chrome Sole Leather

After heavy stock for sole leather has been chrome tanned, it is washed and given a light retanning with vegetable-tanning materials in the drum, a rapid process requiring only a few hours. It is then dried. In some processes,

the leather is subsequently waterproofed by dipping it into hot, molten greases, which penetrate completely through the leather, causing a considerable amount of discoloration. Because of the grease present, pigment finishes applied to it after the greasing operation do not adhere to the surface with sufficient vigor to be practical. Orthmann conceived the idea of finishing the leather before greasing, with a pigment finish impervious to the grease, and then immersing the leather in the molten greases. After the greasing operation, any grease adhering to the surface of the finished leather can readily be wiped off. Being applied before greasing, the pigment finish adheres with great tenacity and the pigment hides any discolorations in the leather below. This method proved to be quite successful in practice, producing a waterproof leather of pleasing color. Orthmann applied for a patent covering the method and product in 1928 and was granted U. S. patent 1,865,783 in 1932. A vertical section of chrome sole leather is shown in Fig. 222 of Chapter 12 (p. 383).

Harness Leather

In making harness leather, the tanning operations are essentially the same as those for sole leather through the rockers and layers; but from this point on, the operations are quite different. In making sole leather, except in the manufacture of flexible sole leather, the tanner attempts to produce a firm and solid piece of leather without much flexibility. He uses extracts, sugars, salts, etc. both to give him the necessary yields of leather and to impart properties desired in sole leather. The uncombined extracts and the sugars cause the fibers to cohere, and give the leather a firmness, which is desired. He is careful not to use too much of oils or greases, because they keep the fibers from cohering and make the leather more flexible. In order to convert firm sole leather into flexible sole leather, he simply washes out the soluble matter that glues the fibers together and adds greases. On the other hand, the tanner of harness leather desires great flexibility and strength and so he avoids loading the leather with extracts and sugars and obtains his gains by stuffing it heavily with greases.

Upon coming from the layers or tanning drums, the first operation is to reduce the content of water-soluble material in the harness leather so that it can be fatliquored properly. Put a pack into a drum and fill the drum to the hollow gudgeon with water at 100° F. and run for 2 hours. Then take the barkometer reading of the liquor in the drum; if it is below 8°, haul out the stock. If it is above 8°, run off half of the liquor and refill the drum with water at 100° F. Repeat this until the stock is essentially in equilibrium with a liquor having a barkometer reading not over 8°. Then haul out the stock. The waste liquors from this operation may be run to the leach house.

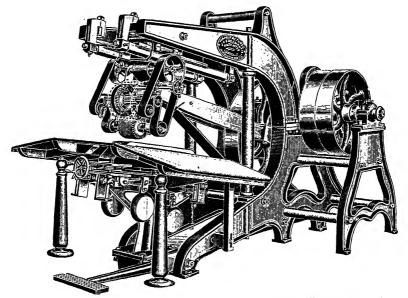
After this operation, press the leather to give it a water content of about 50 per cent, running the liquor from the press to the leach house. Then run the stock in a dry drum to open it up, and then split the heavier areas to level the stock and shave the shanks, heads and bellies. Then fatliquor.

Fatliquoring

Put a pack of 1000 lbs. shaved weight into a drum, start it running, and add 90 lbs. of chamois moellon degras, 30 lbs. of sulfonated cod oil and 9 gals. of water at 150° F., and run for 20 min. Then haul out the stock and hang to dry very slowly, taking from 3 to 5 days to complete the drying and never allowing the temperature to exceed 85° F. After the leather is dry, it may be stored until ordered out.

Stuffing

Make up the dry leather into lots of 700 lbs. dry weight each. Dip each side into water at 100° F. just long enough for it to absorb 50 per cent of its dry weight of water. Then pile the sides down and cover them over so that they will retain the moisture. Allow them to condition, or sammy, for 24 hours. Then put a pack into a stuffing drum like that shown in Fig. 300 of Chapter 15, start running and raise the temperature inside the drum to 115° F. This may take as long as 15 min. because the leather heats slowly. Then add a mixture of 40 lbs. of tallow, 40 lbs. of paraffin wax, 80 lbs. of stearine and 3 lbs. of light mineral oil at a temperature of 125° F., and run 20 min. At the end of this time, all the stuffing mixture should be taken up by the leather and the leather should be hauled out. Hang the leather to cool for about 2 hours; then set out each side very thoroughly both on grain and flesh on a drum setting-out machine like that shown in Fig. 257 (p. 440). Then set out the grain surface thoroughly on a harness setting-out machine, hang up the sides over night and reset the grain. Then hang to dry under such conditions that it takes about 8 days for the leather to become dry. Then pile the leather to condition for 3 days.



Courtesy Woburn Machine Co.

Fig. 407. Whitening and Buffing Machine.

Buffing

Because this leather has been stuffed, it cannot be buffed satisfactorily on an ordinary buffing machine with Carborundum paper, and so it is buffed on a special whitening and buffing machine like that shown in Fig. 407. The bladed cylinder of this machine is shown in detail in Fig. 273 (p. 452) as the whitening cylinder. The grain surface of the leather is then dampened with water at 110° F. It is then fed into the whitening machine, in which

the whitening cylinder works over it with a series of strokes, while the operator shifts the position of the side so that the entire area is finally buffed on the grain side. The buffed grain surface is then dyed the desired color by hand.

Blacking

For black leather, the buffed surface is first swabbed with a $2\frac{1}{2}$ per cent solution of soda ash and allowed to dry. The dye solution is made by dissolving 6 lbs. of logwood crystals and 7 lbs. of nigrosine in 10 gals. of boiling water, cooling, adding 1 gal. of aqua ammonia and diluting to 50 gals. The dye solution is applied to the leather by means of a seasoning and blacking machine, like that shown in Fig. 353 of Chapter 16. After the coating has dried, the leather is passed through a second time to get a coat of a 2 per cent solution of copperas. It is then hung to dry slowly. The leather is then given one of the finishes described for vegetable-tanned calf leather and rolled.

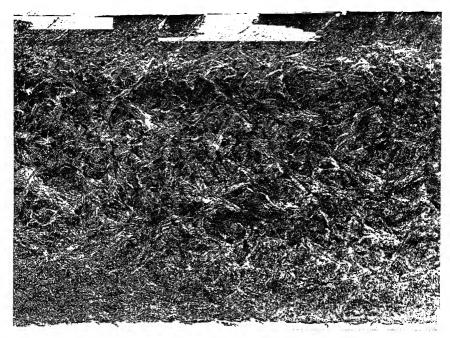


Fig. 408. Vertical Section of Vegetable-tanned Harness Leather.

Location: butt.

Thickness of section: 30 microns, or 0.00118 inch.

Magnification: 14 diameters.

Waterproofing

The dry leather is dipped for 30 min. in molten paraffin wax at about 140° F. and is then hung in a chamber at 140° F. for 30 min. After this it is hung to cool. The flesh side is then buffed on the whitening machine and the excess paraffin is removed from the grain side by hand slicking. A hand slicker is shown in Fig. 296 of Chapter 15. The leather may then be refinished. A vertical section of harness leather is shown in Fig. 408.

Miscellaneous Leathers

Belting leathers are made very much like harness leathers except for the stuffing. As a rule, belting leathers are given less than one-half as much grease and the grease is softer and of lower melting point. A good piece of harness leather may contain as much as 30 per cent by weight of greases and a good piece of belting leather may contain as little as 10 per cent. On the other hand, a good piece of sole leather may contain as little as 3 per cent.

A good piece of vegetable-tanned sole leather may contain as much as 33 per cent of water-soluble matter, consisting of uncombined tanning materials from the yards and of added extracts, sugars, salts, etc. Belting and harness leathers usually contain only from 12 to 14 per cent of water-soluble matter, and practically all of this comes from the yard liquors, none being deliberately added; in fact, the uncombined tanning materials from the yards left in the leather are actually reduced by washing prior to stuffing.

Saddle leathers and strap leathers are often made like harness leather up to and including the fatliquoring operation, without stuffing, but are then set out thoroughly and finished like vegetable-tanned calf leathers, as described in Chapter 17.

The addition of extracts and sugars to vegetable-tanned leathers makes them firmer and less flexible, which is desired in sole leather. Because it also increases the yield of leather, there is a temptation to load the leather with all that it can absorb. This is dangerous, however, in that it tends to make the leather brittle. The writer was once given a problem to solve that bears on this point. A shoe manufacturer had purchased a lot of sole leather that appeared to be of excellent quality and had made up thousands of pairs of shoes with it, which had been sent to retail stores all over the country. After a time, the shoes began to be returned in overwhelming numbers because of the cracking of the soles after less than a day's wear. The writer examined the leather by analysis and microscopic observation and found it to be perfectly normal except for a greater amount of sugar than is usually present in sole leather. He found it possible to eliminate the trouble from the new shoes simply by holding the soles under the tap and allowing water to flow over them for a minute. After drying and refinishing, the tendency for the soles to crack had entirely disappeared. The trouble was due entirely to an excessive amount of sugar in the grain layer gluing the fibrils together so that they ruptured when the sole was flexed. It was fortunate for the tanner that the trouble in this case could be corrected so easily, because he might have been liable to the extent of the value of the shoes, which was many times that of the selling price of the sole leather.

Waterproofing Sole Leather

This is a method applicable not only to vegetable-tanned sole leather, but to many kinds of heavy vegetable-tanned leathers. There is a considerable demand for shoes with soles waterproofed without loading them with heavy greases and waxes. Sole leather can be so waterproofed by incorporating into it vulcanized linseed oil. A tanner can make his own vulcanized lineed oil, but he should do it in a well ventilated hood because of the irritating properties of sulfur monochloride.

Weigh 100 lbs. of raw linseed oil into a copper kettle and add, a little at a time, 15 lbs., 7 oz. of sulfur monochloride (Dow Chemical Co.) so that it takes at least an hour to add it all. Stir well while adding and measure the

temperature frequently. If it rises above 200° F., stop the addition and allow to cool. Add at such rate that the temperature never rises above 212° F. After all has been added, stir vigorously and allow to stand exposed to air for 3 days, with occasional stirring to allow the acid fumes to escape. Then add 92 lbs. of light paraffin oil, 9 lbs. of petrolatum and 25 gals. of naphtha of specific gravity 0.74, and mix well.

To waterproof sole leather, it is merely necessary to dip the dry leather into this solution until it penetrates completely as shown by the cessation of air bubbles coming from the leather. If less of the material is desired in the leather, it is necessary merely to make an appropriate dilution of the material with naphtha. Sometimes the shoe manufacturer does his own waterproofing after the soles have been cut.

This material can be used to advantage in stuffing many varieties of leather to increase their waterproofness.

References

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 Procter, H. R., "Principles of leather manufacture," 2nd ed. D. Van Nostrand Co., New York, 1922.
- Rogers, A., "Practical tanning," Henry Carey Baird & Co., New York, 1922.
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Chapter 19

The Properties of Leather

Leather serves many and varied useful purposes. Its relative value for any purpose is determined by its *properties*, or characteristics. In a shoe, it must have such properties that it can be made to conform to the shape of the foot; it must provide the foot with protection against mechanical damage and with comfort in all kinds of weather; it must provide proper ventilation and yet



Fig. 409. Vertical Section of Hairy Leather for Loom Straps Made from Heavy Italian Steer Hides.

Location: butt.

Thickness of section: 30 microns, or 0.00118 inch.

Magnification: 12 diameters.

it must keep the foot reasonably dry; it must have strength and resistance to abrasion; it must have a pleasing appearance; it must also have the ability to maintain its valuable properties during the life of the shoe. In some kinds of work, leather must possess insulating properties against electrical currents or against heat and cold.

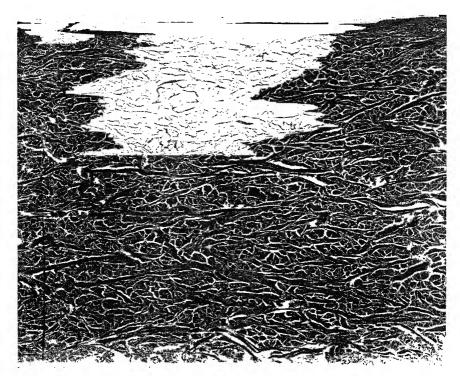


Fig. 410. Vertical Section of Raw-hide Picker Made from Hide of Indian Buffalo.

Location: back.

Thickness of section: 30 microns, or 0.00118 inch.

Magnification: 13 diameters.

Industrial development has reached such a stage that a manufacturer of a new material of commerce would not get very far in offering it to industry unless he listed the values of each of its important properties. A list of these values of properties would be sufficient to rule it out for many uses, thus saving much valuable time in excluding tests for purposes for which it could never be used, and permitting concentration of effort on tests for purposes for which the values of its properties indicated great promise. But leather is an ancient material of commerce, and all too often tanners take it for granted that its properties are so well known that it is not necessary even to measure their values. Probably this unscientific attitude is chiefly responsible for the tanners' failure to develop new uses for leather when their own business is being jeopardized by more scientific manufacturers developing new substitutes for leather.

Values of the important properties of leather are variable, and it is the tanner who varies them. The values of the properties of any kind of leather are very different from those of the original hides or skins, and the tanner is responsible for the differences. Compared to the modern chemical industries, the leather industry has been moving backward for the past two decades,

and certainly partly for the reason that it has been unable to offer lists of values of the properties of the various leathers from which engineers might select those that would meet specifications for various purposes. The shoe manufacturer still buys most of the leather that is made, and substitutes for leather are being used in shoe manufacture to an ever-increasing extent. The manufacturers of substitutes have made far more progress than the tanner in finding new uses for leather.

As recently as 1926, the editor of "International Critical Tables" advised the writer that this great work on the properties of all important substances would have to go to press without any data on leather unless the writer would gather some at once. As a result, he immediately obtained typical samples of 18 different kinds of leather, measured their properties and submitted the data. These are the only data on leather in this great international work, which provides engineers throughout the world with data on the properties of substances.

The properties of leather are determined by (1) its physical structure; (2) its chemical composition; and (3) the mechanical work done on it. A tanner selects the physical structure when he selects the hides or skins for any given purpose, and he changes the chemical composition in his tannery operations. He modifies the properties to the various mechanical operations. Although no two hides



Fig. 411. Vertical Section of Furniture Leather (Vegetable-tanned Cowhide).

Location: back.

Thickness of section: 30 microns, or 0.00118 inch.

Magnification: 65 diameters.

or skins are exactly alike, it is also true that the value of each property need not be an absolute one, but merely one with a maximum and minimum value; usually the permissible range is large enough to take care of natural variations in any one class of stock. Having selected structures of raw stock within reasonable limits, he can learn how to control chemical composition and how to perform the mechanical operations necessary to bring the important properties within the limits required.

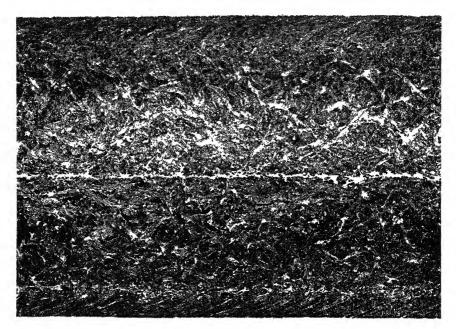


Fig. 412. Vertical Section of Heavy Belting Leather (Two Steerhides Cemented Together).

Location: back.

Thickness of section: 30 microns, or 0.00118 inch.

Magnification: 10 diameters.

Physical Structure

Even a layman would not select a sheepskin to make sole leather, but he would have to learn to differentiate between steer hides and cow hides. Then he would have to learn to distinguish between the different kinds and grades of steer hides available on the market.

The structures of the different types of raw stock are shown and described in considerable detail in Chapter 1. The changes in structure as the stock passes through the tannery are shown in the subsequent chapters. One effect of difference in chemical composition is shown by comparing Fig. 174 (p. 318) with Fig. 214 (p. 373). Both pieces of leather are from the same original skin, which was cut in two along the backbone line, one side being chrome tanned and the other vegetable tanned. The pictures were taken of leather from exactly corresponding points on either side of the backbone. Both sides had the same



Fig. 413. Vertical Section of Basketball Leather (Vegetable-tanned Cowhide).

Location: back.

Thickness of section: 30 microns, or 0.00118 inch.

Magnification: 33 diameters.



Fig. 414. Vertical Section of Football-helmet Leather (Vegetable-tanned Steer Hide).

Location: back. Thickness of section: 30 microns, or 0.00118 inch. Magnification: 29 diameters.

thickness and area before tanning, but after finishing the chrome-tanned side had an area of 5.4 sq. ft. and an average thickness of 2.4 oz. (0.96 mm.), while the vegetable-tanned side had an area of 6 sq. ft. and an average thickness of 3.2 oz. (1.27 mm.). The structures of the two sides are decidedly different, primarily because of differences in chemical composition, and to a lesser extent because of differences in mechanical treatment.

Another effect of difference of chemical treatment upon structure can be seen by comparing Fig. 307 (p. 493) with Fig. 308 (p. 494) in Chapter 15. Here the marked difference is due to a slight difference in fatliquoring.

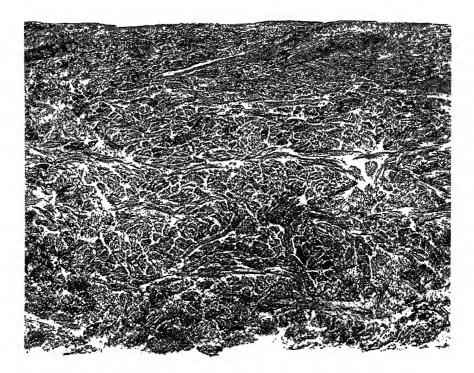


Fig. 415. Vertical Section of Horsehide Baseball Leather (Alum-tanned).

Location: shoulder.

Thickness of section: 20 microns, or 0.00079 inch.

Magnification: 50 diameters.

Structures of most of the common types of leathers have already been shown throughout the book. Fig. 409 shows a section of hairy leather used for loom straps in the cotton mills. It is made from heavy Italian steer hides. The hair is not removed, but it is bleached before tanning. As tanning material, only such materials are used as give low yields, such as gambier. It is heavily oiled, but must not feel greasy. It must maintain its life and resilience after an enormous number of flexings. Similar types of leather with the hair left on are made for round belting, such as that used on sewing machines.

Fig. 410 is raw Indian-buffalo hide as used in making the very hard "pickers"

used in various cotton mills. It is passed through the normal beamhouse operations, but is not tanned at all.

Fig. 411 shows a typical section of top-grain furniture leather consisting of the grain split of a vegetable-tanned cow hide. This leather is finished with a heavy coat of pigmented plastic finish and embossed.



Fig. 416. Vertical Section of Garment Leather (Chrome-tanned Sheepskin).

Location: butt.

Thickness of section: 30 microns, or 0.00118 inch.

Magnification: 48 diameters.

Fig. 412 shows a section of heavy, cemented belting. Vegetable-tanned steer hides are split to uniform thickness and then cemented flesh to flesh. This makes a heavy, durable and flexible belt and both sides of the belt are grain sides.

Fig. 413 shows a section of vegetable-tanned basketball leather made from cow hide. It is split to the desired thickness and embossed. It shows only one full node of the pebbled design of the embossing plate. Intercollegiate football leathers are similar, but they are thicker and are taken only from the butts of choice steer hides for the best balls.

Fig. 414 shows a section of football helmet leather made from vegetable-tanned steer hide. This leather must be very tough, but it must be flexible enough to permit molding into a helmet. After the helmets are made, they are often coated with lacquer pigment finishes in the school colors.

Fig. 415 shows a horsehide baseball leather. It is made from selected horse fronts and is alum tanned. Many baseballs are made also from kips, which are either alum-tanned alone or are tanned with Calgon and retanned with alum. Although horsehide is still official for major-league balls, the writer has demonstrated in hundreds of tests, both in the laboratory and in actual play, that kips are more durable than horsehides.



Fig. 417. Vertical Section of Vegetable-tanned Water-buffalo Hide.

Location: back.

Thickness of section: 30 microns, or 0.00118 inch.

Magnification: 67 diameters.

Fig. 220 (p. 000) shows a section of sheepskin boxing glove leather. Chrometanned sheepskins are ideal for this purpose. Fig. 416 shows a section of sheepskin garment leather that is chrome-tanned. The tendency for sheepskins to separate into grain and flesh layers is not a disadvantage for this kind of leather, because softness and great flexibility is a requirement for coat leathers and the looseness of structure of the sheepskin is really an advantage.

Fig. 417 shows a section of leather made from the water buffalo. The hides are imported from China in the dry state and vegetable tanned for many of the purposes for which cowhides are used. The grain surface has an interesting pattern that makes it popular for hand bags and the leather is sometimes embossed for the cheaper grades of footballs and basketballs.

Fig. 418 shows a section of white kid leather for women's shoes. It is a

goatskin that was lightly chrome-tanned, bleached with syntans and then treated with barium chloride followed by sodium sulfate to precipitate white barium sulfate in the outer layers of the skin. It was then finished with a plastic, and heavily pigmented with titanium dioxide to produce a pure-white leather. It must be remembered that all the sections of skin and leather whose photomicrographs are shown in this book were photographed with light transmitted through the sections. Since the barium sulfate and titanium dioxide pigments are relatively opaque and do not transmit the light, they show black in the picture, although actually they are very white. The heavy black line at the top of the picture is titanium-dioxide pigmented coating of finish and the dark, wide band in the lower part of the picture is the barium sulfate precipitated in the skin.

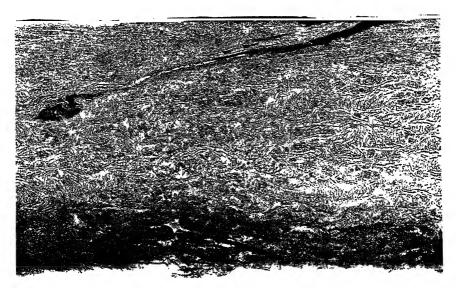


Fig. 418. Vertical Section of White Kid Leather (Chrome-tanned Goatskin).

Location: butt.

Thickness of section: 30 microns, or 0.00118 inch.

Magnification: 62 diameters.

Fig. 419 shows a section of workmen's glove leather made from chrometanned cowhide bellies. Similar types of gloves are also made from splits.

Fig. 420 is a section of black suède leather made from calf slunks; that is, the skins of unborn calves. This leather is worn flesh side out. A velvety nap is produced on the flesh side by buffing while damp on an emery wheel, as described in Chapter 16.

Fig. 421 shows a section of the once very popular buck leather for both men's and women's shoes. It is made from split, chrome-tanned cowhides. The grain is buffed to produce a nap and it is then dusted with colored talcum powers.

Fig. 422 shows a section of typical shell cordovan leather sometimes used in the uppers of men's shoes. It is made from vegetable-tanned horse butts split through the middle of the shell or glassy layer characteristic of the butt of a horse hide. The leather is finished on the split side. By comparing Figs. 187

and 188 [p. 339 and 341] the difference in structure between vegetable-tanned horse fronts and horse butts can be seen.

Fig. 423 shows a section of vegetable-tanned shark leather used widely for toe-caps for boys' shoes. It has the greatest resistance to abrasion of any commercial leather, although great resistance to abrasion is common to all fish skins because they have no thermostat mechanism and, instead of glands which are removed in the beamhouse operations, they have densely packed masses of collagenous tissues.

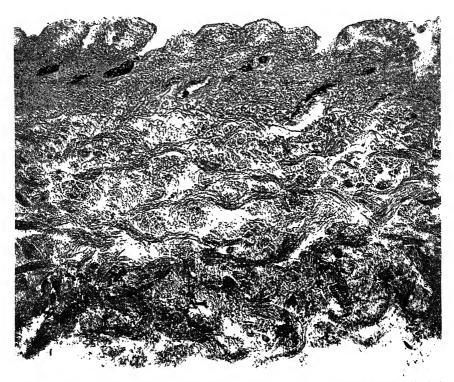


Fig. 419. Vertical Section of Workmen's Glove Leather (Chrome-tanned Cowhide Belly).

Location: belly.

Thickness of section: 30 microns, or 0.00118 inch.

Magnification: 71 diameters.

Fig. 424 shows a section of black kangaroo leather, a favorite for the uppers of baseball and other athletic shoes because it is extremely tough and durable and yet of very light weight.

With all the photomicrographs appearing in this book, the tanner is given a very comprehensive picture of the structures of hides, skins and leathers used in quantity. Discussions of less common types have purposely been omitted in order to give fuller discussions of the more important matters involved in modern practice in leather manufacture.

Chemical Composition

Although the properties of leather are determined chiefly by structure, they are enormously influenced by chemical composition and mechanical handling, and this is something that the tanner can do something about. For example, he can cut a heavy steer hide into two sides and convert one into a firm and solid piece of finders' leather and the other into a soft and stretchy piece of very heavy glove leather. The properties of the two sides of leather would be vastly different, and yet he could give a hide one or the other simply by differences in chemical treatment and in mechanical operations.



Fig. 420. Vertical Section of Black Suède Leather (Chrome-tanned Calf Slunk).

Location: butt.

Thickness of section: 30 microns, or 0.00118 inch.

Magnification: 75 diameters.

The tanner can adjust the chemical composition of the leather he makes within certain limits, and each adjustment has an influence on the physical properties of the leather. Since it is desirable to have as a guide, a list of chemical compositions of various leathers known to be satisfactory, the writer has prepared such a list in Table 50. It does not include every kind of leather, but a sufficient variety so that the tanner can select the one that most nearly resembles the type he is making and from it to get a rough idea of the proportions of fat, water-soluble matter, combined tannin and chromic oxide that his leather might reasonably contain. No fixed chemical composition can be given as best for any type of leather because, in order to get the best results, chemical composition would have to be varied according to the chance solidity of structure of a hide and other factors.

To show one of the many uses to which Table 50 can be put, let us consider the

manufacture of both vegetable-tanned sole leather and vegetable-tanned football leather. Both leathers are made from plump steer hides and both are vegetable-tanned. The properties desired in these two kinds of leather are very different. For sole leather to have the firmness required, it must have a low fat content and a large amount of water-soluble material of the nature of uncombined tanning extract. The greater the amount of uncombined extract in the leather, the firmer it will be; if too much is added, the leather will actually become brittle. For football leather to have great flexibility, tearing resistance and stretch, it must have a high fat content and a low content of water-soluble extract. It will be

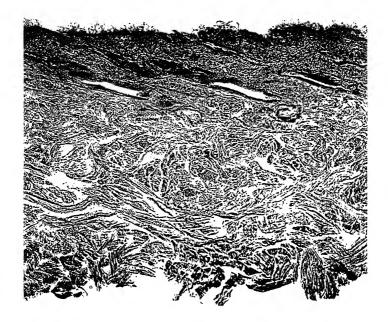


Fig. 421. Vertical Section of Buck Side Leather (Chrome-tanned Split Cowhide).

Location: butt.

Thickness of section: 30 microns, or 0.00118 inch.

Magnification: 75 diameters.

noted that the sole leather has a fat content of only 3.37 percent, whereas the football leather has a fat content of 17.19 percent. Sole leather has a water-soluble content of 33.35 percent and football leather one of only 6.72 percent.

Some tanners have erroneously believed that a high content of *combined* tannin makes the leather very firm and solid. Actually, leather becomes softer as its content of combined tannin increases, if all other factors remain the same. In practice, when leather is given more extract in order to increase the combined tannin, the leather becomes firmer only because of the increasing amount of *uncombined* tannin. This can easily be shown by taking two pieces of sole leather, one with high and one with low combined tannin, and washing them both thoroughly to remove the water-soluble matter. After drying, it will be found that the one of higher combined tannin will be the softer. It will be noted that the satisfactory sole

leather has only 18.12 percent of combined tannin and the satisfactory football leather 23.55 percent. The satisfactory vegetable-tanned calf leather that must be soft contains 27.40 percent of combined tannin.

On an average, 100 lbs. shaved weight of leather dries out to about 50 lbs. of air-dry leather. In fatliquoring football leather to get about 18 percent of fat in the air-dry leather, the tanner would use about 9 percent of actual oil on shaved weight. If the leather to be fatliquored were unusually solid and tight in structure, he would have to use more fat to get the desired flexibility, and he should also wash it more thoroughly before fatliquoring in order to make it softer; with looser leather, he would use less fat and wash less thoroughly.



Fig. 422. Vertical Section of Shell Cordovan Leather (Vegetable-tanned Horse Butt).

Location: butt.

Thickness of section: 30 microns, or 0.00118 inch.

Magnification: 75 diameters.

Complete analyses are not given in Table 50 because it seemed in the best interest to keep it simple to avoid confusion. In chrome-tanned leather, the acidity is very important, but it is not so much the percentage of acid in the leather as it is the ratio of the acid to chrome that is important. In general, the greater this ratio, the firmer and smoother will be the leather; if carried to an extreme, the leather will be tinny. Chrome-tanned leather is also very sensitive to fat; a small

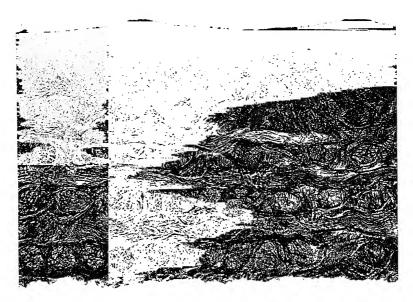


Fig. 423. Vertical Section of Vegetable-tanned Shark Leather.

Location: butt.

Thickness of section: 30 microns, or 0.00118 inch. Magnification: 75 diameters.

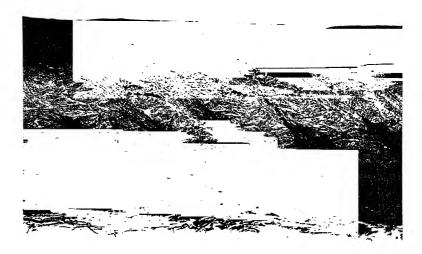


Fig. 424. Vertical Section of Chrome-tanned Kangaroo Leather.

Location: butt.

Thickness of section: 30 microns, or 0.00118 inch. Magnification: 75 diameters.

Table 50. Chemical Composition of Various Satisfactory Leathers in Percent by Weight.

					Water-	Com-	
Vind of looth	***			Hide	soluble	bined	Chromic
Kind of leather	Water	Fat	Ash	substance		tannin	oxide
Bag (vegetable cow)	7.57	3.78	0.28	55.64	5.87	26.49	0.00
Basketball (vegetable steer)	8.65	16.65	0.63	43.69	8.41	21.70	0.00
Belting (vegetable steer)	8.86	11.37	0.23	41.73	13.96	23.85	0.00
Belting (vegetable steer, gambier)	9.69	15.98	2.28	42.49	25.33	6.12	0.00
Boxing glove (chrome sheep)	8.29	15.57	4.86	58.08	1.52	11.93	2.77
Buck (chrome cow)	14.10	2.10	10.60	69.60	0.50	3.60	5.30
Calf (chrome-tanned)	15.10	4.79	7.70	63.16	1.47	4.78	5.54
Calf (vegetable-tanned)	11.34	9.90	0.75	42.39	8.25	27.40	0.00
Cordovan (vegetable horse butt)	10.00	18.60	0.20	40.10	8.70	21.80	0.00
Deerskin (chrome-tanned)	13.04	10.10	5.53	66.79	0.52	2.03	4.68
Elk side (chrome-tanned cow)	12.80	6.74	3.94	71.46	1.35	1.13	3.41
Football (vegetable-tanned steer)	8.80	17.19	1.41	42.47	6.72	23.55	0.00
Furniture (vegetable-tanned cow)	9.28	5.88	0.64	51.30	8.24	24.06	0.00
Garment (chrome horse front)	5.08	26.19	3.66	52.34			3.34
Garment (chrome-tanned sheep)	13.72	16.33	4.02	53.44	0.16	12.43	3.21
Gasket (chrome-tanned cow)	10.72	9.58	3.40	31.60	1 40	2 2:	0.83
Glove (chrome cow belly)	8.94	26.27	8.30	47.33	1.43	8.91	2.40
Glove (chrome cow split)	12.46	22.86	11.00	47.15	2.18	4.95	1.98 3.30
Glove (chrome horse front) Hairy (heavy vegetable steer)	7.53	18.14 13.82	9.81	53.68	1.14 6.32	9.71 14.56	0.00
Harness (vegetable-tanned steer)	11.29		1.03 0.20	51.66 34.09	14.20	14.45	0.00
Kangaroo (chrome-tanned)	7.94 12.00	29.07 11.30	8.40	62.70	0.80	5.10	6.00
Kid (glazed chrome)	9.85	7.86	2.90	71.97	2.58	2.66	2.43
Kid (lining chrome)	17.80	3.66	6.66	59.89	1.90	9.26	5.03
Patent colt (chrome-tanned)	12.00	5.10	6.80	60.40	1.00	9.10	3.60
Patent kid (chrome-tanned)	11.80	6.60	7.00	54.00	0.60	12.20	3.60
Patent side (chrome-tanned cow)	8.51	5.51	3.80	61.78	2.88	15.28	2.58
Picker (raw buffalo)	12.90	2.22	1.81	83.12	0.00	0.00	0.00
Pigskin belt (vegetable-tanned)	14.47	3.27	0.44	44.39	11.88	24.98	0.00
Shark (vegetable-tanned)	12.20	6.90	0.30	45.40	7.00	28.40	0.00
Shearling (chrome-tanned)	7.32	26.68	3.81	54.42	4.66	4.17	0.34
Shearling (vegetable-tanned)	10.68	13.62	3,34	49.93	13.72	10.43	0.00
Sheepskin lining (vegetable)	10.90	6.10	0.30	50.00	2,30	17.40	0.00
Side upper (chrome-retanned cow)	15.10	20.40	4.50	44.60	0.90	15.20	2.40
Side upper (chrome-tanned cow)	13.49	3.48	4.58	71.84	1.66	0.16	3.93
Sole (chrome-retained horse butt)	10.01	30.72	4.21	43.01	2.04	8.31	3.55
Sole (chrome-retanned steer)	13.99	20.57	3.71	51.24	1.63	5.72	3.24
Sole (chrome-tanned steer)	10.70	21.77	4.73	58.24	0.70	0.63	4.15
Sole (vegetable-tanned steer)	9.67	3.37	3.01	34.48	33.35	18.12	0.00
Suède (chrome-tanned calf slunk)	12.70	7.10	8.90	55.10	0.90	15.80	5.40
Split (chrome-tanned cow)	7.20	20.25	14.63	52.50	3.11	3.49	3.04
Waterproof side upper (chrome cow)	9.19	27.28	1.06	47.92	2.01	12.30	0.82
Waterproof sole (vegetable steer)	6.30	11.55	1.47	32.50	25.47	21.51	0.00
Workshoe upper (chrome cow)	8.03	20.60	2.00	45.33	7.88	16.74	0.78
White kid (chrome-tanned)	7.45	4.16	24.19	55.25	11.79	2.97	0.68

increase in fat may make it too soft. Larger percentages of fat are necessary for chrome-tanned leather that has been retanned with vegetable-tanning materials. In general, vegetable-tanned leathers require more fat than chrome-tanned leathers. When large proportions of fat are used on chrome-tanned leathers, the characteristic properties of glove leathers are obtained.

The analyses represented in Table 50 are from cuttings from the portions most valuable for the purposes for which the leather was to be used, but they include the full thicknesses of the leathers. Chemical composition varies, however, at different depths below the grain surface, as shown in Table 51.

In each case, the choice part of the finished leather was taken and split into 5 layers. The thickness of each split is given in ounces; it will be recalled that 1 oz. equals & inch. Analyses made in this way give much more information than can be obtained by analyzing only the full thickness of leather. Practically all finished leathers vary in composition at different depths below the grain surface. In chrome-tanned calf leather, the bulk of the fat is contained in the outer layers; that found in the middle layer is only the natural animal fat. The sulfonated oils used combine with the leather and do not spread over the surfaces of the wet fibers during drying. The neutral oils used in vegetable-tanned calf leather spread and so we find appreciable quantities of fats in the middle layers. In the chrometanned calf, the middle layer contains the largest percentage of sulfuric acid

Table 51. Composition of Various Leathers at Different Depths Below Grain Surface.

Table 31. Composition of various.	2000011010				
Chrome-tanned Calf Thickness of split in ounces. Water Fat Hide substance Sulfuric acid. Sodium sulfate Chromic oxide. Aluminum and iron oxides. Chlorides (sodium plus hydrogen). Combined tannin	Grain Layer 0.33 10.4 16.1 53.0 2.0 0.2 6.0 3.6 0.0 8.7	2nd Layer 0.50 12.3 4.7 64.9 3.9 0.3 6.9 1.8 0.4 4.8	3rd Layer 0.83 14.2 0.7 72.5 4.8 0.2 6.4 0.4 0.8 0.0	4th Layer 0.55 14.6 2.4 70.8 4.3 0.2 6.1 0.5 0.5	Flesh Layer 0.55 11.6 11.1 60.6 2.2 0.1 5.4 1.5 0.0 7.5
Vegetable-tanned Calf				0.01	0.60
Thickness of split in ounces. Water Fat Hide substance Sulfuric acid. Aluminum and iron oxides. Water-soluble organic matter Combined tannin	0.60 9.6 19.4 35.9 0.7 2.5 7.7 24.2	0.71 10.9 14.3 42.8 0.7 0.9 12.2 18.2	1.16 12.3 7.0 48.2 0.3 0.4 13.8 18.0	0.81 12.3 9.9 46.2 0.4 0.6 14.1 16.5	0.60 10.6 13.4 42.1 0.3 1.2 10.0 22.4
Vegetable-tanned Russet Side					
Thickness of split in ounces. Water Fat Hide substance Sulfuric acid. Aluminum and iron oxides. Water-soluble organic matter Combined tannin.	2.14 13.6 11.0 39.3 0.8 0.2 7.9 27.2	1.89 13.9 7.0 42.9 0.9 0.0 6.9 28.4	1.51 13.7 4.3 45.4 1.1 0.0 7.8 27.7	2.02 14.1 2.6 47.8 1.1 0.0 6.5 27.9	1.26 13.6 5.6 45.0 1.1 0.0 6.9 27.8
Vegetable-tanned Harness					
Thickness of split in ounces Water Fat Hide substance Sulfuric acid. Barium sulfate (weighting material) Water-soluble organic matter. Combined tannin.	4.54 9.0 38.3 25.2 0.2 5.3 6.2 15.8	1.89 12.5 16.9 39.8 0.2 0.0 8.8 21.8	1.41 12.2 16.5 40.3 0.3 0.0 9.4 21.3	1.89 12.3 20.6 37.2 0.2 0.0 8.4 21.3	2.82 9.0 33.9 27.9 0.4 4.5 7.0 17.3
Vegetable-tanned Oil Skirting					
Thickness of split in ounces. Water Fat Hide substance Sulfuric acid Aluminum and iron oxides. Water-soluble organic matter Combined tannin	2.52 11.8 8.4 39.8 0.6 0.1 15.5 23.8	3.78 12.8 3.9 45.0 0.8 0.1 15.8 21.6	1.26 13.1 3.6 46.2 0.7 0.1 16.8 19.5	1.26 13.0 5.1 45.3 0.7 0.1 15.2 20.6	2.52 11.6 10.1 41.4 0.6 0.4 14.2 21.7

because the neutralizing agents used in the operations after tanning do not penetrate the leather completely.

In the vegetable-tanned calf, more sulfuric acid is found in the outer layers because it was added after tanning in the bleaching operation and did not penetrate completely through the leather. The water-soluble organic matter is greatest in the middle layer because it penetrated there during tanning and the subsequent washings removed it most thoroughly from the outer surfaces.

In the chrome-tanned calf, the combined tannin is present only in the outer layers, because the sumac and other mordants used in dyeing do not penetrate very deeply into the leather. In harness leather, the greatest proportion of combined tannin occurs in the middle layer. In fatliquoring, uncombined tannin is removed only from the outer layers, leaving more in the middle layer to combine slowly with the hide substance on long standing. The loading of this leather with barium sulfate was purely on the surface, as none is found except in the outer layers.

All determinations of water are likely to vary according to the relative humidity of the atmosphere of the laboratory or place they are kept prior to analysis.

	Chrome-tanned Calf		Vegetable-tanned Calf	
Water	13.0	14.8	11.6	10.9
Fat	5.2	6.5	10.8	15.1
Hide substance	71.4	66.9	41.8	38.4
Sulfuric acid	3.3	1.8	0.8	0.6
Sodium chloride	0.5	0.4		
Chromic oxide	3.1	3.2		
Aluminum and iron oxides	0.5	0.6	0.6	8.0
Water-soluble organic matter	_		7.1	5.7
Combined tannin	3.0	5.8	27.3	28.5

Table 52. Differences in Chemical Composition of Butt and Belly Areas of Calfskins.

Because water evaporates from the surface, the water contents of the middle layers are usually highest.

The chemical composition of a skin also varies over its area, which is the result partly of differences in thickness and partly of differences in looseness of structure. For areas of the same degree of tightness of structure, in fatliquoring,

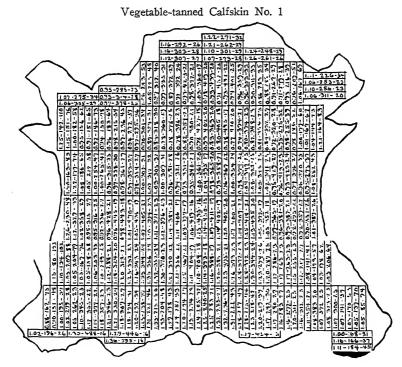


Fig. 425. Chart Showing Variation in Thickness, Strength and Stretch of a Typical Vegetable-tanned Calfskin Over Entire Area.

Test strips cut 1×6 inches in the positions indicated. In each strip, the number to the left is the thickness of the strip in millimeters; the middle number is the tensile strength in kilograms per sq. cm.; and the number to the right is the percent stretch under a load of 225 kilograms per sq. cm. of leather cross-section. 1 millimeter=2.52 ounces. 1 kilogram per sq. cm.=14.2 lbs. per sq. in. A load of 225 kilograms per sq. cm. =14.2 lbs. per sq. in.

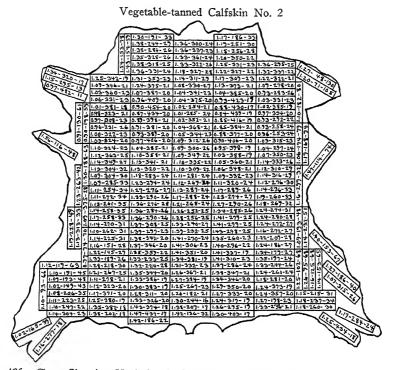


Fig. 426. Chart Showing Variation in Thickness, Strength and Stretch of a Typical Vegetable-tanned Calfskin Over Entire Area.

Test strips cut 1×6 inches in the positions indicated. In each strip, the number to the left is the thickness of the strip in millimeters; the middle number is the tensile strength in kilograms per sq. cm.; and the number to the right is the percent stretch under a load of 225 kilograms per sq. cm. of leather cross-section. 1 millimeter=2.52 ounces. 1 kilogram per sq. cm.=14.2 lbs. per sq. in. A load of 225 kilograms per sq. cm.=14.2 lbs. per sq. in.

the skin tends to take up the same percentage of fat per unit area. For example, if the shoulder has a thickness of 2½ oz. and the butt has a thickness of 3¾ oz. and if the butt is found to contain 7.0 percent of fat, the shoulder will usually contain 9.1 percent of fat. The same rule applies to other materials which do not completely penetrate the leather.

However, for areas of the same thickness, those of looser structure tend to take up more material than those of tighter structure. When skins are being washed, the areas of looser structure give up their water-soluble substances more readily than areas of tighter structure. The bellies of calfskins are usually of the same thickness as the butts, but they are of much looser structure. The effect of structure upon chemical composition is shown in Table 52 for the butt and belly areas of a chrome-tanned calfskin and a vegetable-tanned calfskin.

Although the belly and butt areas were of the same thickness in each skin, the belly areas took up more fat and combined tannin than the butt areas, but contained less water-soluble matter because of the greater ease with which it is removed by washing.

Strength and Stretch

The tensile strength of leather and its resistance to stretching vary greatly over the entire area of a skin. These properties vary also according to the kind and age of the animal, the kind and degree of the tannage, the chemical composition and the degree of splitting.

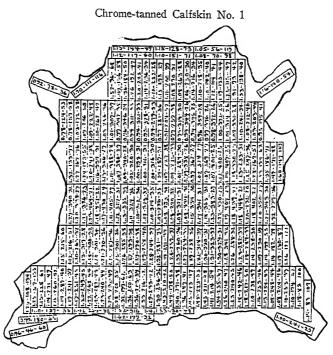


Fig. 427. Chart Showing Variation in Thickness, Strength and Stretch of a Typical Chrome-tanned Calfskin Over Entire Area.

Test strips cut 1×6 inches in the positions indicated. In each strip, the number to the left is the thickness of the strip in millimeters; the middle number is the tensile strength in kilograms per sq. cm.; and the number to the right is the percent stretch under a load of 225 kilograms per sq. cm. of leather cross-section. I millimeter=2.52 ounces. 1 kilogram per sq. cm.=14.2 lbs. per sq. in. A load of 225 kilograms per sq. cm. = a load of 3195 lbs. per sq. in.

To show the very important effect of location on the skin, it seems best to give complete results for calfskins. The entire areas of two vegetable-tanned calfskins and two chrome-tanned calfskins were cut into strips 1 by 6 inches each with a die. In one skin of each tannage, the strips were cut parallel to the backbone line, and in the other they were cut perpendicular to it. Before cutting into strips, each skin was kept in an atmosphere of 50 percent relative humidity and then each strip was tested at once. The thickness of each strip was measured immediately before testing with the sensitive Randall & Stickney gauge shown in Fig. 202 (p. 357). The tests were made on a Scott vertical machine with the jaws set 4 inches apart. This machine was equipped with a recording device for showing the

stretch as a function of the load. Since each strip was exactly I inch wide, its thickness in inches was also a measure of its cross-section area in square inches.

Altogether 894 strips were tested. The results are shown to best advantage in Figs. 425 to 429, inclusive, taken from "The Chemistry of Leather Manufacture," pages 1056 to 1059, inclusive. The location of each strip on the skin is shown and

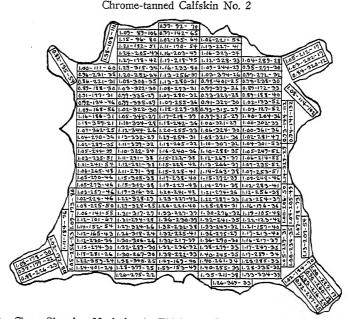


Fig. 428. Chart Showing Variation in Thickness, Strength and Stretch of a Typical Chrome-tanned Calfskin Over Entire Area.

Test strips cut 1×6 inches in the positions indicated. In each strip, the number to the left is the thickness of the strip in millimeters; the middle number is the tensile strength in kilograms per sq. cm.; and the number to the right is the percent stretch under a load of 225 kilograms per sq. cm. of leather cross-section. 1 millimeter=2.52 ounces. 1 kilogram per sq. cm.=14.2 lbs. per sq. in. A load of 225 kilograms per sq. cm. =a load of 3195 lbs. per sq. in.

on the diagram of each strip, three numbers are marked. The number to the left is the thickness of the strip in millimeters. The middle number is the tensile strength in kilograms per sq. cm. of leather cross-section. The number to the right is the percent stretch under a load of 225 kilograms per sq. cm. of cross-section. In "The Chemistry of Leather Manufacture," the metric system of measurements was used because the book was written for chemists. In order to convert thickness into ounces, simply multiply the value given for millimeters by 2.52. To convert tensile strength into lbs. per sq. in. of cross-section, simply multiply the value given for kilograms per sq. cm. by 14.2. A load of 225 kilograms per sq. cm. is the same as a load of 3195 lbs. per square inch.

In order to show graphically how strength and stretch vary as one moves from one part of the skin to another, the values taken from Figs. 425 and 426 are plotted in Figs. 429 and 430, respectively.

All these values plus thousands of other values available to the writer were then used to make the graph shown in Fig. 431, which it would be well to memorize because it represents the distribution of strength, stretch and solidity of structure more or less common to all hides and skins.

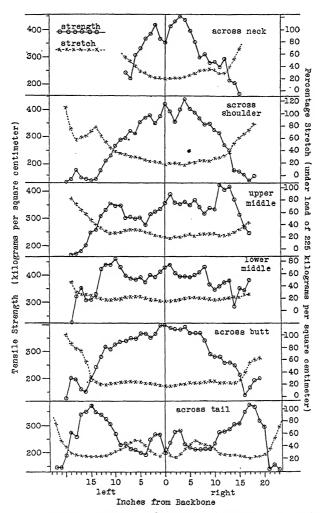


Fig. 429. Charts Showing Variations in Strength and Stretch of a Typical Vegetable-tanned Calfskin Over Entire Area. Pull exerted in direction parallel to line of backbone. Values taken from Fig. 421.

As a matter of interest, the maximum, minimum and average values for the tests on the four calfskins are given in Table 53.

Thousands of tests have shown that there is little to choose between the tensile strength of chrome-tanned calf and that of vegetable-tanned calf, and that essentially the same results are obtained whether the strips are cut parallel or

Table 53. Maximum, Minimum and Average Values for the Tests Whose Values Are Given in Figs. 421 to 424, Inclusive.

			nned Calf	Vegetable-tanned Calf		
Number of strips tested		skin #1 206	skin # 2 197	skin #1 251	skin #2 240	
Transci of Strips tested		200			-10	
Thickness in ounces	maximum minimum average	4.08 2.32 2.95	3.86 2.07 2.82	3.78 1.86 2.67	3.93 2.12 2.97	
Tensile strength in lbs. per sq. in.	maximum minimum average	6589 653 3678	5694 1264 3550	6930 1136 4345	6844 682 4118	
Percent stretch under load of 3195 lbs. per sq. in.	maximum minimum average	168 20 43	132 12 40	133 15 33	130 13 29	

(Where the tensile strength was less than 3195 lbs. per sq. in., the stretch value was obtained by extrapolation and is, therefore, of theoretical significance only.)

perpendicular to the backbone line. The tighter leather is set out in any one direction, the less will be the stretch in that direction. The greater the pressure applied in smooth-plating, the less will be the thickness and the greater will be the tensile strength per unit cross section.

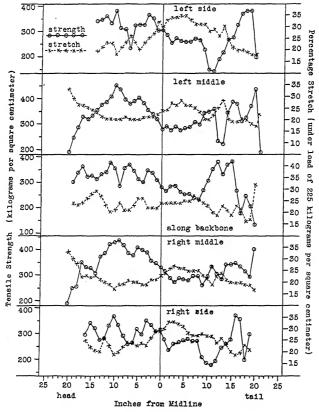


Fig. 430. Charts Showing Variations in Strength and Stretch of a Typical Vegetable-tanned Calfskin Over Entire Area. Pull exerted in direction perpendicular to line of backbone. Values taken from Fig. 422.

Effect of Splitting

The tensile strength of leather is not uniform throughout its thickness. The uppermost layer, which contained the thermostat mechanism in the living skin, is relatively very weak, nearly all of the strength of the leather being in the reticular layer. Any reduction of thickness of leather by splitting thus tends to alter its tensile strength and may either increase or decrease it per unit cross section, depending upon the strength of the part removed. It is thus apparent that the extent to which leather has been split or shaved in process of manufacture

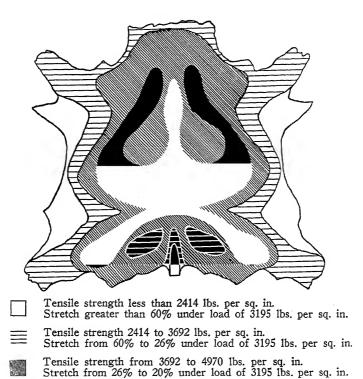


Fig. 431. Chart Showing Variation in Strength and Stretch of Typical Calfskins Over Their Entire Areas.

Tensile strength greater than 4970 lbs. per sq. in. Stretch less than 20% under load of 3195 lbs. per sq. in.

will affect the results of any tests in which tensile strength is the dependent variable. Wilson and Kern have prepared two charts showing how the strength of chrome- and vegetable-tanned calf leathers varies as the grain or flesh layer is reduced in thickness by splitting.

A number of representative skins of finished vegetable- and chrome-tanned calf leathers were selected. On either side of the backbone of each skin, and with length parallel to it, an area 6×25 inches was cut so that the inner edge was about 4 inches from the backbone and the ends equal distances from the head and tail ends of the skin. This area was then cross cut into twenty-five strips each 1×6 inches, num-

bered consecutively. The odd numbered strips were tested for tensile strength and resistance to stretch. All leather when tested was in equilibrium with an atmosphere of 50 percent relative humidity. The results were used to calculate the strengths of the even numbered strips, which were assumed to be the average of the strengths of the adjoining strips. For example, the average strength of strips 3 and 5 was assumed to be the strength of 4. In general this will be true, so that reliable results may be assured if the test is repeated several times. Each even numbered strip was split on a band knife machine into two layers. In 2 the splitting was done so that the grain layer was 10 and the flesh layer 90 percent of the total thickness; in 4 the grain was 20 and the flesh 80 percent of the total thickness; and so on. The strength of each split was then measured and compared with the calculated strength of the unsplit strip.

For each kind of leather the entire experiment was repeated several times to insure reliable results, and these are plotted in Figs. 432 and 433. Each figure has a pair of cross lines and three curves, one of which represents the sum of the other two. The curves represent strength per unit width, not cross section. However, the strength per unit cross section can be obtained from the figures and its variation is indicated by the relation of the curves to the cross lines. Where the curve is above its corresponding cross line the strength per unit cross section has been increased by splitting and where below, it has been decreased. Cutting away the grain layer to a depth less than 48 percent for the vegetable-tanned leather or less than 22 percent for the chrome increases the strength per unit cross section of the remaining flesh layer, because the grain portion of the leather is so much weaker than the flesh portion.

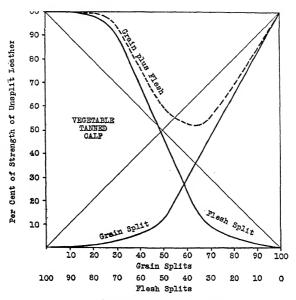
Splitting always causes a loss in strength per unit width and the sum of the strengths of the two splits is always less than the strength of the unsplit strip. This is shown by the uppermost curve in each figure. The distance of this curve from the 100 line gives the total loss in strength of the leather due to splitting. If the chrome leather is split into two layers of equal thickness, the grain layer will be only 26 and the flesh layer 16 percent as strong as the unsplit leather, making a total loss of strength of the original leather of 58 percent.

This excessive loss in strength of the flesh layer is the result of the severing of the fibers in splitting, which is likewise responsible for the great loss in strength of the leather as a whole. It does not indicate weakness of the reticular layer compared with the thermostat layer. On the contrary, cutting away the thermostat layer (one-sixth of the total thickness) increases the strength of the flesh layer per unit cross section, while the grain layer suffers a loss with the removal of any amount of flesh layer.

The greater looseness of structure of the chrome leather is responsible for the greater maximum total loss of strength, 60 percent for the chrome against only 48 percent for the vegetable-tanned leather. This is also shown in the greater weakness of the chrome flesh layers. In the chrome leather the flesh is weaker than the grain when it is less than 53 percent of the total thickness; in the vegetable-tanned leather the flesh is the weaker only when it is less than 41 percent of the total thickness.

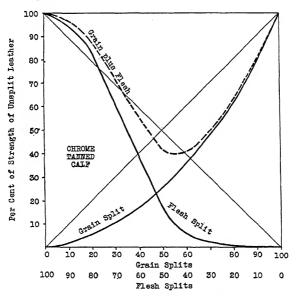
The writer's experiments upon heavy leathers indicate that the effect of splitting is similar in kind but not in quantity to that here described. It must be remembered that the ratio of thickness of thermostat layer to reticular layer decreases with increasing thickness of the original skin.

The resistance of the leather to stretch was found to vary directly with the strength. Measurements were made of the load in kilograms required to stretch



Per Cent of Total Thickness

Fig. 432. Relative Strengths of Splits of Vegetable-tanned Calf Leather Compared to Strength of Unsplit Leather. Average tensile strength of unsplit leather=4601 lbs. per sq. in. Average thickness of unsplit leather=2.29 oz.



Per Cent of Total Thickness

Fig. 433. Relative Strengths of Splits of Chrome-tanned Calf Leather Compared to Strength of Unsplit Leather. Average tensile strength of unsplit leather: 3554 lbs. per sq. in. Average thickness of unsplit leather: 2.62 oz.

each strip to 1.25 times its initial length and this value was called R, or the resistance to stretch. Splitting caused a percentage decrease in the value of R for both grain and flesh splits identical with the percentage decrease in strength. Thus Figs. 432 and 433 may be used to indicate the resistance of the leather to stretch simply by calling the ordinates "percent of resistance to stretch of the unsplit leather."

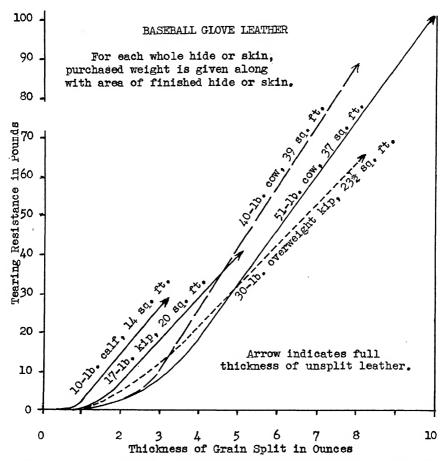


Fig. 434. Effect of Splitting upon Tearing Resistance of Baseball Glove Leather Made from Packer Hides and Skins of Different Purchased Weights.

Fleming, working in the writer's laboratories, made a similar study of the effect of splitting upon the resistance of leather to tearing. He used a side upper leather which was chrome tanned, then retanned in hemlock bark extract, stuffed with wool grease, moellon degras and currier's wax, and finished for heavy work shoes. Strips 1×6 inches were slit along the midline to the three-inch mark and torn on the Scott machine by clipping the slit ends in the jaws of the machine

and noting the load required to tear the strip. The unsplit leather required a load of 53 lbs. at a thickness of 5.04 oz. Splitting caused a decrease in resistance to tearing practically identical with the decreases in tensile strength shown in Figs. 432 and 433. The effect of splitting is evidently similar upon tensile strength, resistance to stretching and resistance to tearing.

It is a general rule that hides and skins have maximum strength when not split at all. If a leather of given weight is required, it would naturally be assumed that the weight of raw stock to select for maximum strength would be that requiring least splitting. That this assumption is not always true was shown by the following experiment. The writer was trying to determine the weight of raw stock that would produce maximum tearing resistance in baseball glove and mitt leathers of 5 to 6-ounce weights. He selected good packer stock of 10, 17, 30, 40 and 51-lb. weights and converted them into glove leathers. Comparable areas of each from the butt were split into many grain layers of the thicknesses shown in Fig. 434.

Each piece to be tested was cut into a square exactly 2×2 inches. A slit was made from the middle of one side to the center of the square. The jaws of the testing machine were brought together and the piece was clamped into both jaws so that the slit was between them. The device for recording stretch was attached and the machine was started. As the jaws pulled apart, the leather began to tear, and an increasing load was required until the tearing had proceeded far enough so that the fibers were pulling together; then the load decreased to continue the tearing, which was evidently due to the increasing leverage created as the distance from the jaws to the point of tearing increased. The point of maximum load was naturally taken as the nearest approach to the true value for tearing resistance. The results shown in Fig. 434 were obtained by the writer's assistant, Stewart L. Shehee.

For thicknesses up to 3 oz., the assumption holds perfectly, the strongest leathers being those of lightest initial weight. For a thickness just under 5 oz., the split 40-lb. cow is stronger than either the 17-lb. kip or the 30-lb. overweight kip. The highest point on each curve represents the full, unsplit thickness of the leather. For thicknesses above 5 oz., the strength increases as the ratio of total area to unsplit thickness, which is greatest for the 40-lb. cow and least for the overweight kip.

Effect of Relative Humidity

The water content of leather varies with the relative humidity of the atmosphere with which it is in equilibrium, and it has a measurable effect upon the strength and stretch of the leather. Wilson and Kern studied this effect on both chrometanned and vegetable-tanned calf leathers. In each experiment, they cut a strip of leather 7 by 25 inches from one side of a skin, with its length running parallel to the line of the backbone, its sides equidistant from backbone and belly edges, and its ends equidistant from head and tail ends of the skin. Each strip was then subdivided into 21 smaller strips of 7-inch length and numbered from 1 to 21 beginning at the head end. These strips were allowed to reach equilibrium with an atmosphere of 50 percent relative humidity; they were then cut with a die to exactly 1 by 6 inches, and the thickness of each strip was measured.

All the odd-numbered strips were kept in a chamber at a relative humidity of 50 percent. Each of the even-numbered strips was kept in a separate chamber at a definite relative humidity, ranging from 0 to 100 percent in steps of 10 percent. After conditioning in this way for 46 days at 68° F., each strip was

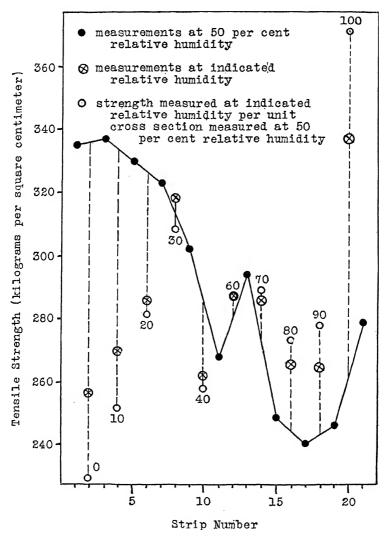


Fig. 435. Effect of Relative Humidity upon the Tensile Strength of Chrome-tanned Calf Leather. (To convert values to lbs. per sq. in., simply multiply them by 14.2.)

measured for length, width and thickness and then tested for strength and stretch on a Scott machine equipped with a recording device for showing stretch as a function of load. As soon as each strip was tested, it was analyzed for water content.

The results for the odd-numbered strips of the chrome-tanned calfskin are plotted in Fig. 431 in the form of a curve. In order to convert the values given into lbs. per sq. in., simply multiply by 14.2 the values given for kilograms per sq. cm. Since the tests were all made at 50 percent relative humidity, the curve may be taken as showing the variation in tensile strength from head to tail of the

original strip. In the method employed, it is assumed that the points for the even numbered strips would all have fallen on the curve, if the strips had been in equilibrium with an atmosphere of 50 percent relative humidity at the time of breaking.

In comparing the results at different relative humidities, a complication arises in the change of volume of the leather with relative humidity. The volume of a given mass of chrome leather at zero relative humidity may increase 30 percent or more by the absorption of water when brought into equilibrium with saturated air. For this reason, if the effect of relative humidity upon equal masses of leather is to be measured, the cross sections must be measured at the same relative humidity and the load required to break the strips measured at the indicated relative humidity.

In Fig. 435 the even numbered tests are recorded in two ways. First they are listed in kilograms per sq. cm. measured at the indicated relative humidity. But one cc. of the leather at zero relative humidity represents a greater mass of leather substance than one cubic centimeter at 50 percent relative humidity, making the value of tensile strength at zero relative humidity relatively greater than if given in terms of the same mass of leather as at 50 percent relative humidity. Similarly the tests made at relative humidities greater than 50 percent give tensile strength values lower than if given in terms of the mass of leather at 50 percent relative humidity. So the tests are also recorded in terms of the area of the cross-section which the leather had at 50 percent relative humidity. These values give the true effect of relative humidity by eliminating the variable volume change with relative humidity.

The percentage gain or loss in tensile strength with changing relative humidity can be calculated by comparing the value for a given relative humidity with that of the intersection of a vertical line passing through the point with the continuous curve for 50 percent relative humidity. For example, at zero relative humidity the tensile strength is 229 kilograms per sq. cm. A vertical line through this point intersects the curve at a value of 333. Lowering the relative humidity from 50 percent to zero has thus caused a percentage loss in tensile strength of 100-229/3.33 or 31.3.

The essential data for the chrome leather are given in Table 54. The water content increases from 1.95 to 70.37 grams per 100 grams of dry leather, with increasing relative humidity from zero to 100 percent. With a drop in relative humidity from 50 percent to zero, the area of the cross-section shrinks 10.6 per-

Table 54.	Effect of	Relative	Humidity	upon	the	Strength	and	Stretch	of	Chrome-
			tanned C	alf Le	athe	27".				

Percent Cain

					nt Gain	Fercent
					n Strength	Increase
	Grams	Cross-sect	ion of Test	at Indica	ated R. H.	or Decrease
	Water	Str	ip at ——	Per	Unit -	in Stretch
Percent	Per 100	Indicated	50 Percent	Cross S	ection at	Under Load
Relative	Grams Dry	R. H.	R. H.	Indicated	50 Per Cent	of 225 Kg.
Humidity	Leather	(Sq. Cm.)	(Sq. Cm.)	R. H.	R. H.	per Sq. Cm.
0	1.95	0.211	0.236	-23.7	-31.3	2 decrease
10	8.97	0.229	0.246	-19.0	-24.0	8 decrease
20	11.66	0.230	0.242	-10.3	-13 <i>.</i> 7	5 decrease
30	14.81	0.242	0.251	+ 1.7	– 0.7	8 decrease
40	16.07	0.257	0.261	- 8.0	– 8.4	2 decrease
50	18 <i>.</i> 75	0.264	0.264	0.0	0.0	no change
60	20.64	0.269	0.269	+ 2.4	+ 3.3	19 increase
<i>7</i> 0	23.47	0.277	0.274	+ 5.2	+ 7.4	15 increase
80	27.41	0.295	0.287	+ 8.4	+13.0	17 increase
90	32.64	0.299	0.284	+ 8.8	+15.5	17 increase
100	70.37	0.313	0.284	+28.4	+42.8	8 increase

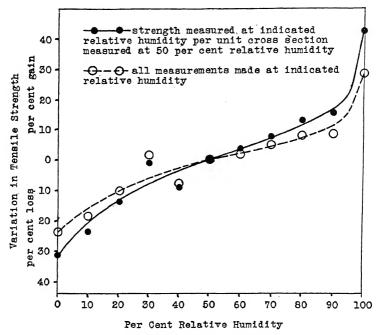


Fig. 436. Variation in Tensile Strength of Chrome-tanned Calf Leather with Changing Relative Humidity of the Atmosphere.

cent and with rise in relative humidity from 50 to 100 percent, the area increases 10.2 percent. With the area at 50 percent relative humidity taken as unity, the extreme area change is 20.8 percent. The tensile strength varies from a loss of 31.3 percent at zero relative humidity to a gain of 42.8 percent at 100 percent relative humidity, a total change of 74.1 percent. These results are plotted in Fig. 436.

In Table 54 figures are also given for the percentage change in stretch as measured at the indicated relative humidity under a load of 225 kilograms per sq. cm. as measured at 50 percent relative humidity. The change in stretch

Table 55. Effect of Relative Humidity upon the Strength of Vegetable-tanned Calf Leather.

Percent Relative Humidity	Grams Water Per 100 Grams Dry Leather	Percent Gain or Loss in Tensile Strength
0	4.21	6.9 loss
10	8.46	2.7 loss
20	10.62	3.3 loss
3 0	11.71	4.3 gain
40	13.00	0.3 gain
50	16.08	0.0
60	1 7. 76	2.0 loss
<i>7</i> 0	19.00	0.3 loss
80	22.71	2.0 loss
90	25.29	5.4 loss
100	30.18	6.1 gain

is too small compared to experimental error to give a clearly defined curve, but it is clear that the leather stretches more easily at higher relative humidities.

The experiments with the vegetable-tanned leather showed the effect of relative humidity on tensile strength to be smaller than the experimental error. This is illustrated in Table 55 where the percentage gain or loss is given as a function of relative humidity. The breaking load was measured at the indicated relative humidity and the area of the cross-section at 50 percent relative humidity. Where the area of the cross section is measured at the indicated relative humidity, the variation in strength is still less. The change in stretch is even less pronounced. The test was repeated on two other skins with essentially the same result, namely, that variation in relative humidity has a negligible effect upon the tensile strength and stretch of this kind of leather.

Two reasons may be assigned to the difference found between chrome and vegetable-tanned leather. The greater strength at higher relative humidities is apparently due to the lubricating value of the absorbed water. The greatest amount of water absorbed by the vegetable-tanned leather was 30.18 against 70.37 for the chrome leather. In addition, the lubricating effect of the water would be less where the leather fibers are more thoroughly lubricated by oil and the vegetable-tanned leather contains approximately three times as much oil as the chrome leather.

Veitch, Frey and Leinbach measured the strength and stretch of three sides of vegetable-tanned kip leather finished without any application of oils, greases, finishing materials or sizes; that is, they were finished in the "crust." On an average, they showed by analysis only 0.2 percent of fat. Measurements were made at relative humidities of 35, 55, and 75 percent. Raising the relative humidity from 35 to 55 percent caused an increase in average tensile strength from 155 to 175 kilograms per sq. cm. and in percent stretch from 32 to 37. In another series, raising the relative humidity from 35 to 75 caused an increase in average tensile strength from 182 to 259 and in percent stretch from 25 to 38.

Effect of Oil Content

Wilson and Gallun made a study of the effect of oil content upon typical specimens of chrome-tanned calf and kid leathers. The effect of splitting was eliminated by using skins that had not been split. The effect of relative humidity was eliminated by keeping it constant at 50 percent. The effect of location was eliminated by making it rigidly comparable for both kinds of leather and selecting a region showing greatest uniformity. The strips were cut from the region midway between head and tail and extending from a point 1 inch from the backbone line to a point 6 inches from it. The strips were cut with a die 1 by 6 inches with their lengths running parallel to the backbone line.

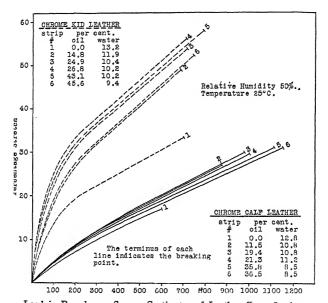
Each strip was degreased with chloroform, soaked over night in a chloroform solution of known strength of neat's-foot oil, freed from chloroform in a current of air for 48 hours, and then kept in an atmosphere of 50 percent relative humidity at 77° F. for 3 days.

The measurements of strength and stretch were made on a standard Scott machine equipped with a recording device. The initial distance between the jaws was fixed at 6 inches. The thickness of each strip was measured just before testing and the water and fat contents were determined immediately thereafter.

Wilson and Gallun made a number of comparative tests, but obtained essentially the same results in all and so published a description of only one. In this test, the calf leather had an average thickness of 1.76 and the kid leather of 2.27 oz. The results are given in Fig. 437.

With increasing oil content, both the leathers show a decreasing tendency to hold water. In a similar series kept at 50 percent relative humidity for 16 days, the same differences in water content were found.

The most outstanding difference is the much greater tendency for the kid leather to stretch, which has long been widely appreciated in a qualitative way from actual wear, which explains why kid shoes lose their shape so much more readily than those of calf. The reason for this greater tendency to stretch is found in the fact that goat skins, like sheep skins, have a structure very much looser naturally than calf skin, which can be seen by examining cross-sections of the raw skins. This loose structure also means that goat skins have less protein matter per unit cross-section, which explains why their leathers are so much weaker than calf leathers, where the latter possess enough oil to overcome the internal friction of the fibers.



Load in Pounds per Square Centimeter of Leather Cross Section.

Fig. 437. Strength and Stretch of Chrome-tanned Calf and Kid Leathers as a Function of Oil Content.

The calf leather increases steadily in strength with increasing oil content, which has but little effect upon the strength of the kid leather. This may possibly be attributed to the difference in fundamental structure of the two skins, but it is not so clear why the tendency to stretch with increasing oil content shows a point of maximum with both leathers beyond which there is an apparent decrease.

Bowker and Churchill made a study of the effect of oils, greases and degree of tannage upon the tensile strength, stretch, and buckle strength of russet harness leather. They found an increasing tensile strength with increasing grease content up to a certain amount above which the strength of the leather decreased. The points were so far apart that the critical amount of grease could not be

determined, but a side with 23.35 percent of grease was weaker than its mate, taken from the same hide, which showed only 10.70 percent of grease. Increasing the duration of the tanning process yielded leather of lower tensile strength, although the longer-time tannage produced a leather more resistant to shear when used with a buckle. They also found that the use of mineral oil did not affect the physical properties of new leather in a manner different from that caused by the use of cod oil.

Effect of Kind of Tannage and Method of Finishing

Bowker studied the effect of kind of tannage and method of finishing on the strength and stretch of leather in connection with the investigations of a special

Table 56. Chemical Composition of Belting Leathers Used in Strength and Stretch Tests.

		getable — Finished		ination _		ome — Finished
XX7-411.1	Rough		Rough	Finished	Rough	rinished
Water solubles	12.67	10.00	4 7 00	00 51	<i>(</i> 7 <i>(</i> 0	CT 07
Hide substance	43.29	39.11	45.88	39.74	67.68	67.37
Grease	3.16	12.61	4.27	17.22	1.85	15.30
Moisture	9.42	8.42	9 . 75	8.05	11.35	11.65
Insoluble ash	0.12	0.08				
Combined tannin	31.34	29.78				
Degree of tannage	72.4	76.1				
Soluble tannins	9.53	7.60				
Soluble non-tannins	3.14	2.40				
Glucose	none	none				
Epsom salts	none	none				
Acid (P & S)	0.42	0.40				
Unsaponifiables	24.0	30.0	10.0	13.0	none	none
Total ash	0.28	0.17	3.49	3.08	7.35	6.86
Total sulfate			2.05	2.04	4.79	4.74
Neutral sulfate			0.47	0.53	0.68	0.63
Sulfuric acid			1.96	1.85	5.03	5.03
Total chlorides			0.05	0.06	0.40	0.51
Chromic oxide			2.83	1.70	6.38	6.00
Aluminum and iron oxides			0.41	0.46	0.34	0.21
Aluminum and Hon Oxides			0.71	0.70	0.07	0.21

(P & S means that Procter & Searle test was used for determining acid.)

Table 57. Effect of Tannage and Finish upon Strength and Stretch of Belting Leathers.

			At Stress	Stretch —	Tensile Strength	
Sample No.	Hide No.	Tannage and Finish	of 2500 Lbs. Per Sq. In.	At Failure	Lbs./Sq. Inch	Direc- tion*
140.	140.					T
1	1	Rough vegetable-tanned	24.3	30.0	2950	L
2	1	Rough chrome-tanned	44.0	53.5	2995	L
3	2	Rough vegetable-tanned	21.3	<i>27.7</i>	2850	С
4	2	Rough chrome-tanned	42.1	51. <i>7</i>	2780	С
5	2 3	Finished vegetable-tanned	13.2	27.4	5250	L
6	3	Finished chrome-tanned	23.1	35. 6	3395	L
7	4	Finished vegetable-tanned	16.4	29.4	4375	С
8	4	Finished chrome-tanned	47.1	56.4	2830	С
9	5	Rough vegetable-tanned	21.9	31.5	3310	С
10	5	Rough combination-tanned	19.6**	27.1	2110	С
11	6	Rough vegetable-tanned	26.0	31.4	2865	L
12	6	Rough combination-tanned	32.7	31.9	2055	L
13	7	Finished vegetable-tanned	15.0	29.7	4840	L
14	7	Finished combination-tanned	20.8	30.9	3505	L
15	8	Finished vegetable-tanned	21.6	36.6	4185	С
16	8	Finished combination-tanned	31.1	43.3	3450	С

^{*} Direction of cutting test pieces. L=Lengthwise, C=Crosswise.
** Result probably too low since only few pieces had a strength of 2500 pounds per square inch.

committee of the American Leather Chemists' Association. Samples of belting leather were furnished by F. H. Small of Graton and Knight Co., Worcester, Mass.

Eight hides were split down the back and tanned as indicated in Table 57 so that comparisons could be obtained on leather from the same hide as to the strength and stretch of vegetable, combination chrome and vegetable, and straight chrome leathers, in both the rough and finished conditions. The leather was furnished in the form of bends. Each bend was cut into pieces approximately 1½ by 6 inches from which a standard ½-inch reduced section specimen was died out. Equal amounts of each type of leather were tested in the crosswise as well as the lengthwise direction of the hide. Physical tests made were for tensile strength in lbs. per sq. in., percent stretch at 2500 lbs. per sq. in. cross-section and percent stretch at failure. The chemical compositions of these leathers are given in Table 56 and the results of the physical tests in Tables 57 and 58.

Table 58. Summary of Results Given in Table 57.

Vegetable -		Combin	ation —	Chrome —		
ugh Fi	nished	Rough	Finished	Rough F	inished	
005	E04E	2055	2505	2005	2205	
					3395	
080	4280	2110	3450	2/80	2830	
25.0		00 =	00.0	44.0	^-	
					23.1	
21.6	19.0	19.6	31.1	42.1	47.1	
30.7	28.6	31.9	30.9	53.5	35.6	
29.6	33.0	27.1	43.3	51.7	56.4	
	905 080 25.2 21.6 30.7	080 4280 25.2 14.1 21.6 19.0 30.7 28.6	ugh Finished Rough 905 5045 2055 080 4280 2110 25.2 14.1 32.7 21.6 19.0 19.6 30.7 28.6 31.9	905 5045 2055 3505 080 4280 2110 3450 25.2 14.1 32.7 20.8 21.6 19.0 19.6 31.1 30.7 28.6 31.9 30.9	ugh Finished Rough Finished Rough F 905 5045 2055 3505 2995 080 4280 2110 3450 2780 25.2 14.1 32.7 20.8 44.0 21.6 19.0 19.6 31.1 42.1 30.7 28.6 31.9 30.9 53.5	

From the results of the physical measurements, Bowker drew the following conclusions:

- 1. The finished vegetable-tanned leather is much stronger than either the finished combination or chrome-tanned leathers.
- 2. The finished vegetable-tanned leather shows less stretch, both at a definite stress and at failure than either the finished combination or chrome-tanned leathers.
- 3. The combination-tanned leather shows the greatest percentage increase in strength due to the finishing process, and the chrome leather the least. The approximate percentage increases are combination 70, vegetable 40, chrome 10.
- 4. The vegetable and chrome rough leathers have about the same strength while the combination is about 30 percent weaker.
- 5. The finished vegetable and chrome leathers are stronger in the lengthwise direction while the finished combination leather is about the same in both the lengthwise and crosswise directions.
- 6. The rough leathers for each tannage have about the same strength and stretch in both directions.
- 7. One marked effect of the finishing process for all tannages is to materially reduce the stretch at a definite stress in the lengthwise direction. In the crosswise direction it remains about the same as for the rough leathers.
- 8. The ultimate stretch is about the same for the finished leathers as for the rough leather with the exception of the finished combination in the crosswise direction which is materially increased and the finished chrome-tanned leather in the lengthwise direction which is materially reduced.

Bowker also studied the effect of the kind of tannage upon the strength and stretch of sheep leathers furnished by E. W. White of A. C. Lawrence Leather Co., Peabody, Mass. The chemical analyses were not given. Table 59 gives the results of the strength and stretch tests.

It will be noted that the sheep leather is much stronger in the lengthwise direction than in the crosswise direction regardless of the type of tannage and

		Average	. At	Stretch — At	Tensile Strength	
Sample*	Tannage**	Thickness Inches	1000 Lbs. Per Sq. In.	Failure Percent	Lbs. Per Sq. In.	Direc- tion***
1	C	0.035		47.0	2915	L
4	С	.038		42.0	3440	L
5	С	.034	25.5	43.8	2440	L
1A	. V	.037		37.2	3325	L
4A	V	.044		36.5	4125	L
5A	V	.038	18.2	35.3	2995	Ļ
2 3	Ç	.039	64.7	90.2	2305	C
	Č	.030		90.0	2120	Č
6	C	.029	***	80. <i>7</i>	1595	C
2A	V	.038	61.4	85.8	2355	Ç
3A	V	.036		76.5	2515	C
6A	V	.031		8 7. 3	1755	C
			Summary			
1A-4A-5A	V	0.040		36.3	3495	L
2A-3A-6A	V	.035		82.9	2280	С
1-4-5	С	.036		44.3	2900	L
2-3-6	С	.032		86.8	1995	С

Table 59. Effect of Kind of Tannage upon the Strength and Stretch of Sheep Leathers.

that the percent stretch is approximately double in the crosswise direction what it is in the lengthwise direction. The finishing methods may have an influence on those properties. The vegetable-tanned leathers are stronger and stretch less than the chrome-tanned leathers.

The effect of the kind of tannage for calf leathers is included in the section above dealing with the effect of location.

Strength, Stretch and Tearing Resistance of Various Satisfactory Leathers

In Table 50 (p. 643), the chemical compositions of a great variety of commercial leathers are given. To the extent that values for strength, stretch and tearing resistance of these leathers are available, they are given in Table 60. These values are not to be considered as standards, but they were all obtained by direct measurements of leathers known to be satisfactory in service. In some cases, the values given represent averages obtained from many hundreds of hides or skins; in others, they represent determinations made on only a single sample.

For any one hide or skin, three samples were taken for testing: one from the shoulder, one from the butt and one from a point intermediate between the other two. The three sets of results are averaged.

Ventilating Properties of Leather

It is well recognized that a foot housed in a compartment impervious to water and air cannot be comfortable, and most people have experienced the discomfort attending the wearing of rubbers for any great length of time. The animal body gets rid of its excess heat by the evaporation of perspiration from the surface of the skin. If the foot is so confined that the perspiration at its outer surface cannot diffuse away or evaporate, it will become hot and uncomfortable. The perspiration inside the shoe tends to maintain a relative humidity of 100 percent in the confined atmosphere. In order to prevent discomfort, the leather of the shoe must remove the water from this inner, humid atmosphere and pass it on to

^{* 1} and 1A, 2 and 2A, etc., sides of the same skin.

^{**} C=Chrome, V=Vegetable.

^{***} Direction of cutting test pieces; L=Lengthwise, C=Crosswise.

Table 60. Strength and Stretch of Various Satisfactory Leathers (See Table 50).

Kind of leather Bag (vegetable cow). Basketball (veg. steer). Belting (gambier steer). Belting (Gambier steer). Belting (Gambier steer). Boxing glove (chrome sheep) Buck (chrome cow). Calf (chrome-tanned). Calf (vegetable-tanned) Cordovan (veg. horse butt) Deerskin (chrome-tanned). Elk side (chrome cow). Football (veg. steer). Furniture (veg. cow). Garment (chrome horse fr.) Glove (chrome cow belly). Glove (chrome cow belly). Glove (chrome horse front) Hairy (veg. steer). Harness (veg. steer). Kangaroo (chrome-tanned) Kid (glazed chrome). Kid (lining chrome). Kid (lining chrome-tanned) Patent colt (chrome-tanned) Patent side (chrome-tanned) Patent side (chrome-tanned) Shearling (veg. tan). Shearling (veg. tan). Shearling (veg. tan). Shearling (veg. tan). Sole (chrome-retan horse). Sole (chrome-retan steer). Sole (chrome-retan steer). Sole (chrome-retan steer). Sole (chrome calf slunk) Sult (veg. steer). Waterproof cale (veg.)	4.28 11.84 12.02 2.32 2.32 2.32 2.35 2.82 5.39 5.62 3.53 2.82 5.70 3.53 2.82 5.70 3.53 2.82 5.70 3.53 2.82 3.55 4.94 12.50 1.86 2.42 2.75 6.48 2.19 6.24 2.19 6.25 1.57 1.59 1.5	Lbs. to break 1 in. width 530 179 1096 483 996 103 1633 240 71 419 475 288 1708 758 117 555 221 40 106 97 480 228 354 370 821 713 555 168 298 510	Tensile strength (lbs. per sq. in.) 4699 2679 5912 2625 2491 2854 4358 6096 1803 6734 5768 5460 1586 6093 2175 5808 3877 5808 3873 7214 5075 2184 1136 1422 2840 4913 4484 2112 1539 3365 3409 2215 3422 2857 2705	% Stretch at 1000 lbs. per sq. in. 15 24 6 7 36 11 8 5 222 226 111 118 121 229 20 12 22 220 12 22 20 12 20 1	% Stretch when grain cracked 38 41 25 18 46 29 28 58 40 27 — 26 37 26 37 25 23 32 — 43 32 25 21 28 34 31 — 30 21 32 36 14 18 49 38 21	% Stretch when leather broke 38 41 25 18 57 29 29 28 58 42 27 60 311 499 23 32 40 599 27 42 40 25 21 39 38 31 40 34 21 32 36 15 28 49 40 21	Tearing resistance (lbs.) 20 14 62 38 4 4 26 20 39 2 17 19 4 4 21 17 15 4 4 62 12 10
Split (chrome-tanned cow) Waterproof upper (chrome) Waterproof sole (veg.) Workshoe upper (chrome) White kid (chrome)			3422 2857 2705 911 4740	17	38	40	- - 3

the outer atmosphere of lower relative humidity. Good shoe leather has the power to do this very effectively.

In attempting to analyze the ventilating power of leather, the author has picked this property as being one of the most important and has devised a method for measuring it. The property has been referred to as "permeability to water vapor."

Permeability to Water Vapor

The essential part of the apparatus used to measure the power of leather to conduct water from an atmosphere of high to one of low relative humidity is shown in Fig. 438. It consists of a small wide-mouth bottle fitted with a screw cap, in which a hole 1.4 cm. in diameter has been cut. The leather sample is cut with a circular die having the same diameter as the two brass disks used—namely, 3.0 cm. (1.18 inch). In the center of each disk a hole is cut exactly 1.27 cm. in diameter which allows an area of exactly 1.267 sq. cm. of leather to be exposed. The leather is placed between these two brass disks and set into the cap as shown. A tightly fitting cork having a hole in its center 1.4 cm. in diameter is then inserted. The cork resting on the rim of the bottle effects a water-tight seal.

Some pure sulfuric acid is put into the bottle and then bottle and acid, without the cap, are weighed. The cap containing the leather is then screwed into place and the whole is placed into an ordinary individual desiccator containing water, and this in turn is submerged in a large Freas thermostat constant to 0.01° C. The

acid inside the bottle tends to maintain an atmosphere of practically zero relative humidity, while the water in the desiccator tends to maintain an atmosphere of 100 percent relative humidity. The only way that water can pass from the outer humid atmosphere to the inner dry one is through the leather. In order to



A—Aluminum screw cap with hole 1.4 cm. diam.

B—Disk of leather sandwiched between two brass disks each with a hole exactly 1.27 cm. (½ inch) diam.

C—Tightly fitting cork with hole 1.4 cm. diam.

D-Bottle of 70 cc. capacity.

Fig. 438. Apparatus to Measure Rate of Passage of Water through Leather from an Atmosphere of High to One of Low Relative Humidity.

determine how much water has passed through the 1.267 sq. cm. of leather area in unit time, it is only necessary to remove the bottle and weigh it with the cap removed. The object in removing the cap before weighing each time is to avoid fluctuations due to the changing water content of the leather and cork. Wilson and Lines used this apparatus in an investigation of the ventilating properties of typical leathers and of the effects of important variable factors.

Effect of Temperature

In studying the effect of temperature two series of these pieces of apparatus were set up. In one series the caps contained disks of vegetable-tanned calf leather all taken from the butt of the same skin. In the other series no leather was used, but the holes in the disks allowed free contact of the wet and dry atmospheres over the area of 1.267 sq. cm. In the leather series, all grain surfaces were exposed to the dry and the flesh surfaces to the wet atmosphere, as would be the case in the wearing of a shoe. The desiccators were placed in thermostats at different temperatures and the bottles were weighed once each day for a week. The gain in weight per day varied only very slightly throughout the week. The results are shown in Table 61 and in Fig. 439.

Table 61. Effect of Temperature upon Passage of Water from an Atmosphere of 100% Relative Humidity to One of Zero Humidity Across an Area of 1.267 sq. cm. through Free Space and through Vegetable-tanned Calf Leather.

Temp	erature (°F.)	Milligrams water per leather	24 hrs. passed through free space	Ratio (%)
5	41	71	98	72
20	68	192	286	67
20 25	<i>77</i>	236	360	66
30	86	328	505	65
35	95	430	660	65
40	104	560	863	65
45	113	765	1214	63

In order to convert milligrams water per 1.267 sq. cm. of leather into ounces per sq. ft. of leather, simply multiply by 0.0258. Thus at a temperature of 77° F. each sq. ft. of leather is passing 6.1 ounces of water per day. The particular leather used in these tests had been finished in such manner as to give it water-repelling properties in shedding rain and yet it passed approximately two-thirds

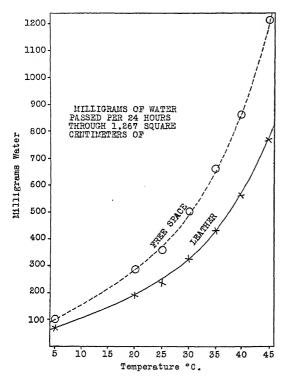


Fig. 439.

Effect of Temperature upon Passage of Water from an Atmosphere of 100% Relative Humidity to One of Zero Humidity through Free Space and through Vegetable-tanned Calf Leather.

as much water as that passing through free space of the same area. This is one of the very important properties of leather that make it so valuable for shoes and garments.

Effect of Relative Humidity

Although the relative humidity of the air inside the shoe during wear tends to be maintained at 100 percent, that of the outside air is very variable. From the description of the thermostat mechanism of the skin given in Chapter 1, it will be appreciated how very important it is for health and comfort that the body never be covered by anything that will stop the continuous evaporation of perspiration. It is important to know how much increasing relative humidity of the atmosphere retards the evaporation of water from the inside of a shoe in wear. When pure sulfuric acid is kept in an enclosed space, it removes all the water from the space above it and tends to maintain an atmosphere of zero humidity. By making appropriate dilutions of the acid, atmospheres of any desired relative humidity can be maintained. Bottles were made up with acid of such concentrations as to maintain relative humidities of 0, 20, 40, 60, 80 and 100 percent,

respectively and the tests were repeated on the same sample of leather at 25° C. The results are shown in Table 62 and Fig. 440.

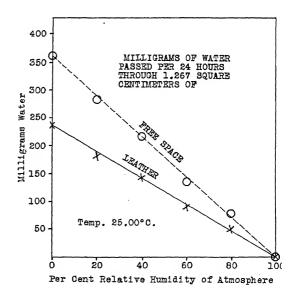
Table 62. Effect of Relative Humidity of One Atmosphere upon Passage of Water into It from an Atmosphere Kept at 100% Relative Humidity Across an Area of 1.267 sq. cm. through Free Space and through Vegetable-tanned Calf Leather at 25° C. (77° F.).

Relative humidity (%)	Milligrams water per i	24 hrs. passed through free space	Ratio (%)
0	236	360	66
20	179	282	63
40	143	217	66
60	91	134	68
80	51	78	65
100	0	0	

The rate of passage of water in both series appears to be a straight-line function of the difference in relative humidity between the two atmospheres, and the ratio of the rate of passage through the leather to the rate of passage through free space appears to be constant at 66 percent at all relative humidities. Since this ratio appears to be independent of temperature and of difference in relative humidity, it can be used as a constant characteristic of any given sample of leather. The writer has used it to indicate the degree of permeability of leather to water vapor and the value for this particular sample of calf leather is 66 percent.

Fig. 440.

Effect of Relative Humidity of One Atmosphere upon Passage of Water into It from an Atmosphere Kept at 100% Relative Humidity Across an Area of 1.267 sq. cm. through Free Space and through Vegetable-tanned Calf Leather at 25°C. (77°F.).



Relative Porosity

The apparatus designed by the writer to measure the porosity of leather is shown in Fig. 441.

A disk of leather is cut with a die 3 cm. (1.18 in.) in diameter, exactly as in the determination of permeability to water vapor, and clamped in the brass receptacle B. D is then screwed so tightly into B that no air can pass through the

system without passing through the leather. The vacuum pump is then run so as to maintain a constant reading of 25 in. on the vacuum gage. The amount of air passing through the leather is measured by the volume of water passing from bottle F to bottle E, which can be read directly from the calibration marks on bottle E. The relative porosity is defined as the number of cc. of air passing through 1 sq. cm. of leather per minute when the gage reading is constant at 25 in.

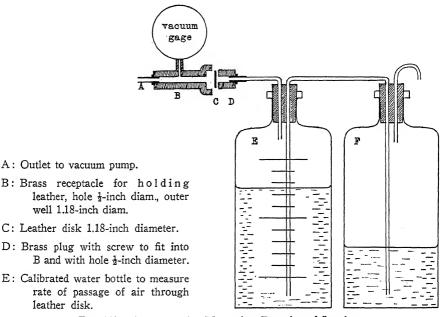


Fig. 441. Apparatus for Measuring Porosity of Leather.

Effect of Oil Content

A series of disks of vegetable-tanned calf leather was completely degreased with chloroform and then soaked in chloroform solutions of neatsfoot oil of different strengths. The disks were then freed from chloroform and used in the tests, after which the oil contents were determined. The results are shown in Fig. 442.

Increasing the oil content of the leather decreases both permeability and porosity, but the nature of the decreases is not the same in both cases, as will be noted by studying the curves in Fig. 442.

Effect of Finishing

Disks of unfinished vegetable-tanned calf leathers were given successive coatings of finishing material, between each of which they were dried and polished with wool. The amount of dry material used in each coating was measured by the weight of the wet coat applied, determined by noting the loss in weight of the bottle containing the finish. In one series, an aqueous solution of casein was used and in the other a solution of collodion in a mixture of alcohol and ether. The results are shown in Figs. 443 and 444.

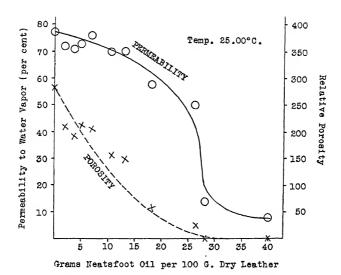


Fig. 442. Effect of Neatsfoot Oil on the Ventilating Properties of Vegetable-tanned Calf Leather.

The amounts of finishing materials used are given in terms of milligrams of dry material per 100 sq. cm. of leather. To convert this into lbs. of dry material per 1000 sq. ft. of leather, simply multiply by 0.0205. For example, where 100 milligrams of dry material was used per 100 sq. cm. of leather, there was used 2.05 lbs. of dry material per 1000 sq. ft. of leather.

Varo, working in the author's laboratories, made a very extensive study of

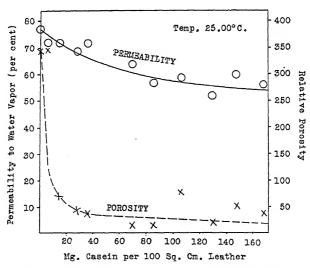


Fig. 443. Effect of Casein Finish on the Ventilating Properties of Vegetable-tanned Calf Leather.

the effects of various finishes and methods of finishing upon the permeability of leather to water vapor and upon its relative porosity. He studied first the effect of glazing colored chrome calf leather to which no finishing material had been applied. The initial permeability value was 88. The first glazing reduced it to 80, the second to 78, and the third to 76. Subsequent graining or boarding did not change this value. The relative porosity was initially 600. The first glazing reduced it to 300, the second to 180, and the third to 170. Subsequent graining brought it back to 250. This work was repeated with the application of a great variety of finishing materials preceding each glazing.

Shellac preparations caused a greater decrease in ventilating properties than protein finishes. Pressure-treated gelatin, gum arabic, soluble starch, and linseed extracts increased the ventilating power over that of leather glazed without finishing. Waxes, sulfonated oils, pigments, dyes, and varnishes all decreased the

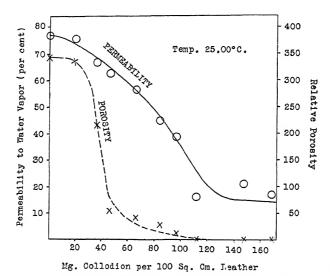


Fig. 444. Effect of Collodion Finish on the Ventilating Properties of Vegetable-tanned Calf Leather.

ventilating properties. The great decrease in ventilating properties caused by lacquers and varnishes in making patent leather was shown to be due primarily to the large quantities applied; when applied in quantities comparable with the amounts of shellac, casein, and other finishing materials ordinarily used on leathers, it caused no greater decrease in ventilating power. The graining or boarding of leathers after finishing and glazing causes an increase in ventilating power, probably because this operation produces tiny breaks in the hardened film of finishing material.

Directional Effects

In making tests with ordinary chrome or vegetable-tanned calf leathers, Wilson and Lines found the permeability to water vapor to be practically the same whether the grain or the flesh side was exposed to the humid atmosphere. With patent leathers, however, a big difference was found. With the flesh side toward the

humid atmosphere, the permeability factor, in one test, was 6, but with the grain side toward the humid atmosphere, it was 20. In other words, the water passed through the leather in one direction more than three times as fast as in the other. This finding is worthy of further study.

In actual wear, two kinds of transmission of water are involved: the passage of water from a humid to a dryer atmosphere and the actual passage of liquid water in contact with the leather. As long as the relative humidity of the outer air is less than 100 percent, it is natural to suppose that water passes continuously from the foot through the leather of the shoe to the outer air. There should never be any back passage because the foot tends to keep the air inside the shoe saturated with water. But when the shoe is brought into direct contact with water, a diffusion of water through the leather will start as soon as the surface has been wetted. In making leather, it is possible to finish it so as to make it very difficult to wet on the grain side without greatly lowering the permeability of the leather to water vapor. This has the practical effect of making a one-way water trap. The moisture from the foot can pass out through the leather quite freely, but liquid water on the outside is kept from entering because of the difficulty of wetting the leather surface. The mechanism by which the water is passed through the leather in the two cases is probably very different.

Ventilating Properties of Various Leathers

The ventilating properties and average thicknesses of a number of commercial leathers are given in Table 63.

Table 63. Ventilating Properties and Thicknesses of Various Commercial Leathers.

Kind of leather Buck (chrome-tanned cow). Calf (chrome-tanned) Calf (chrome-tanned). Calf (chrome-tanned). Calf (chrome-tanned). Calf (vegetable-tanned). Calf (vegetable-tanned). Cold (vegetable-tanned). Cordovan (veg. horse butt). Deer (vegetable-tanned). Garment (veg. sheep). Harness (veg. cow). Hog (chrome-tanned). Hog (chrome-tanned). Kid (glazed chrome). Patent colt (chrome-tanned). Patent kid (chrome-tanned). Patent kid (chrome-tanned). Patent kid (chrome-tanned). Patent kid (chrome-tanned). Sheepskin lining (veg.). Side upper (chrome-cow). Side upper (chrome-retan). Sole (chrome-steer).	2.90 3.86 4.44 13.18 4.66 1.31 1.84 2.42 2.29 3.60 2.42 2.75 2.24 2.19 3.07 5.10	Permeability to water vapor (%) 95 76 70 70 72 70 74 54 75 75 61 76 36 65 70 70 52 70 70 52 4 34	Relative porosity 1183 7892 67 635 383 197 427 421 1750 22 185 249 5 375 0 0 0 1416 2511 369 143 0 43
Sole (chrome steer) Sole (vegetable steer) Solède (chrome calf slunk) Workshoe upper (chrome cow)	12.10 15.93 1.59		
For comparison: White duck	1.54 2.52	. 94 . 0	3380 0

Dimensional Changes in Leather with Relative Humidity

Being engaged in the manufacture of both chrome-tanned and vegetable-tanned calfskins for shoe uppers, Wilson and Gallun had many occasions to study differ-

ences in properties between leathers of the two kinds of tannage. In many tests, they cut calfskins into sides along the line of the backbone and tanned one side of each skin with chrome and the other side with vegetable-tanning materials. They would then have a pair of shoes made from each side at the same time and on the same last. This provided two pairs of shoes for each test. They would wear a left shoe of chrome leather and a right shoe of vegetable-tanned leather for a while and then alternate, wearing a left shoe of vegetable-tanned leather and a right shoe of chrome. They thus established that in the varying climate of Milwaukee the shoes of vegetable-tanned leather were more comfortable and held their shapes better than the corresponding shoes of chrome-tanned leather.

A careful investigation revealed that all shoes change in size with changes in relative humidity of the atmosphere, but that the magnitude of the change is much greater for chrome-tanned than for vegetable-tanned leather. Leather absorbs water very readily from moist air, increasing in volume and in area. It gives up water readily in dry air, shrinking correspondingly in volume and area.

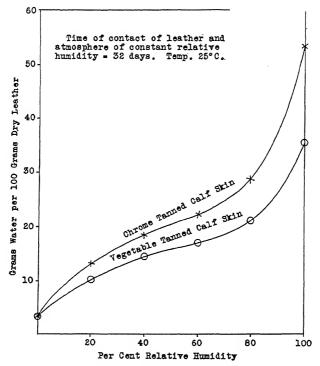


Fig. 445. Effect of Relative Humidity of the Atmosphere upon the Water Content of Chrome-tanned and Vegetable-tanned Calf Leathers.

Wilson and Gallun developed a method for determining this effect quantitatively. Air-tight chambers were set up containing atmospheres maintained at 0, 20, 40, 60, 80 and 100 percent relative humidities, respectively. Strips of finished leather were cut to a standard size when in equilibrium with an atmosphere of 50 percent relative humidity. For each leather being tested, a standard strip was placed in

each chamber of constant relative humidity and left there until it had reached equilibrium; that is, until it underwent no further change in weight or in area with time. The area of each strip was then measured with precision and its water content was determined.

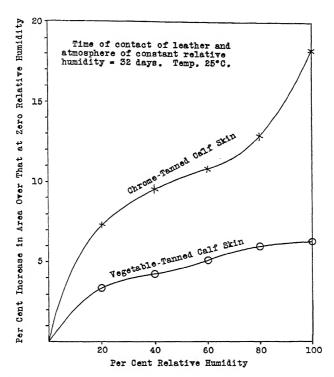


Fig. 446. How the Areas of Chrome-tanned and Vegetable-tanned Calf Leathers Increase with Increasing Relative Humidity of the Atmosphere.

In the chambers at relative humidities below 50 percent, all strips lost weight and shrank in area to increasing extents the lower the relative humidity. In the chambers at relative humidities above 50 percent, all strips gained weight and increased in area to increasing extents the higher the relative humidity.

For comparable sides of finished chrome-tanned and vegetable-tanned calfskins made from the same skin, the results are shown in Figs. 445 and 446. Fig. 445 shows the parts of water per 100 parts of dry leather held by the leather when in equilibrium with atmospheres of different relative humidity. In this test, the strips of leather were kept in the chambers of constant relative humidity for 32 days to make sure that equilibrium was established. At zero relative humidity, both leathers still contained 3.5 parts of water per 100 parts of dry leather; in the case of the chrome leather, this increased with relative humidity to 53.2 against only 35.4 for the vegetable-tanned leather.

Fig. 446 shows the effect of water absorption upon the areas of the strips. The area at zero relative humidity is taken as unity and the percentage increase due to water absorption calculated from this. The curve for the chrome leather is of

Table 64.	Water Contents of Various Leathers after 30 Days' Contact with Atmospheres
	of Different Relative Humidities.

Sample	Kind	Grams	Water	per 100 Relative	Grams Dry Humidity	Leather Perce	After	30 D	ays
No.	of Leather	0	20	40	50	60	80	1	100
1.	Vegetable calf	1.4	10.8	14.0	15. <i>7</i>	17.9	21.2		9.6
2.	Chrome calf	2.1	12.4	18.1	19.5	21.0	27.9		3.4
3.	Glazed kid (C)	2.9	10.6	14.2	15.9	18.1	27.3		2.2
4.	Kangaroo (C)	0.4	9.3	12.6	13.6	15.4	22.8	5	1.7
5.	Cordovan (V)	1.8	<i>7</i> .0	9.8	11.1	11.8	15.6	2	2.9
<u>6</u> .	Buck (C)	2.2	11.7	15.4	16.4	17.4	25.1	4	7.8
7.	Chrome side	1.8	12.1	17.2	19.5	20.8	25.9	5	4.5
8.	Suède (C)	0.3	9.4	13.4	14.5	15.8	20.9	59	9.5
9.	Calf lining (V)	0.9	8.8	12.1	13.5	16.1	19.6	32	2.0
10.	Sheep lining (V)	1.1	8.2	11.3	12.2	14.6	19.6	48	8.4
11.	Shark (V)	2.4	10.2	12.7	13.9	14.3	17.1	38	8.1
12.	Patent side (C)	0.7	8.5	10.4	11.2	12.6	18.5	36	6.9
13.	Patent kid (C)	1.9	10.5	12.7	13.4	14.6	20.7	39	9.5
14.	Patent colt (C)	2.0	9.6	12.4	13.6	15.1	22.7	52	7.5
15.	Heavy chrome	1.2	12.9	15.1	16.8	17.7	21.9	49	9.6
16.	Chrome retan	4.4	12.5	16.4	17.8	18.4	21.1	37	7.8
17.	Vegetable sole	3.4	12.2	17.0	17.1	18.3	21.7	43	3.6
18.	Chrome sole	8.6	14.9	18.1	19.5	20.6	24.5	50	0.4

⁽C) indicates chrome tannage; (V) indicates vegetable tannage.

the same general shape as that for water absorption, with a point of inflection at about 50 percent relative humidity, but that for the vegetable-tanned leather has two points of inflection. This might have been attributed to experimental error were it not for the fact that it occurred also with other vegetable-tanned leathers examined.

The processes were found to be entirely reversible and the rate of approach towards equilibrium similar for the two kinds of leather. When the dry leather is put into a desiccator at 100 percent relative humidity, in the first day it takes

Table 65. Area Change of Various Leathers with Increasing Relative Humidity of the Atmosphere.

		Pe	rcent Increas	se in Are	a with Inc. Above Zero	easing Re	elative
Sample	Kind		Per	cent Rela	tive Humic) 1;+-v	
No.	of Leather	20	40	50	60	80	100
1.	Vegetable calf	3.6	4.2	4.5	4.8	5.5	5.7
2.	Chrome calf	7.7	10.0	10.3	11.5	12.4	16.0
3.	Glazed kid (C)	3.4	4.6	4.8	5.5	7.5	15.6
4. 5.	Kangaroo (C)	5. <i>7</i>	6.9	6.9	7.5	10.9	19.0
5.	Cordovan (V)	2.0	3.0	3.0	3.2	3.4	4.0
6.	Buck (C)	6.7	7.5	7.7	8.8	10.5	14.7
7.	Chrome side	6.7	7.7	8.0	9.2	10.5	15.8
8.	Suède (C)	8.0	10.7	10.9	11.7	11.9	13.8
9.	Calf lining (V)	5.3	6.5	6.7	6.9	7.5	9.2
10.	Sheep lining (V)	4.2	5.5	5.5	5.9	8.2	9.4
11.	Shark (V)	4.0	4.9	5.1	5.3	5.7	8.0
12.	Patent side (C)	5.5	6.3	6.3	6.9	8.6	10.5
13.	Patent kid (C)	5.3	5.9	6.1	6.5	7.1	9.6
14.	Patent colt (C)	4.5	6.3	6.3	6.5	8.2	13.0
15.	Heavy chrome	7.1	8.0	8.0	9.2	10.9	16.9
16.	Chrome retan	6.5	7.7	8.0	8.4	9.0	11.5
1 <i>7</i> .	Vegetable sole	1.0	1.4	2.7	3.0	3.0	5.5
18.	Chrome sole	3.8	4.5	5.9	6.3	7.7	13.0

⁽C) indicates chrome tannage; (V) indicates vegetable tannage.

up 50 percent and in 2 days 60 percent as much water as it will take up in a total time of 1 month, the same being true for either chrome or vegetable leather. Leathers kept over water for a month and then placed over pure sulfuric acid gave up 70 percent of their water the first day and 85 percent by the end of the second day. The changes in area correspond to the changes in water content.

Wilson and Kern measured the increase in area and water content with increas-

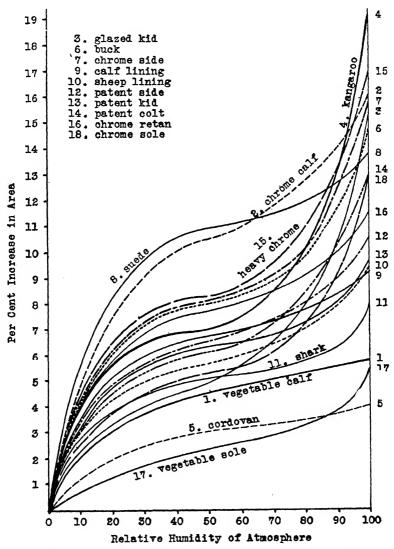


Fig. 447. Percentage Increase in Area of Various Leathers with Increasing Relative Humidity of the Atmosphere.

ing relative humidity of 18 typical shoe leathers. The samples were kept in an atmosphere of 50 percent relative humidity for 6 weeks and were then cut into strips, as in the experiments of Wilson and Gallun, measured for area and weighed. The water content was determined on a portion of each sample; this and the weight of the strip made it possible to calculate the dry weight of the strip. One strip of leather was put into each desiccator above the acid solution and its weight and area were measured at intervals. The desiccators were kept tightly covered except for the moment, at intervals, when the leather was being measured. The temperature was 25° C.

The difference between the weight at any period and the known dry weight of any strip gave the water content. This is shown for the thirty-day period in Table 64. At 100-percent relative humidity, the water content of the vegetable-tanned leathers varied from 22.9 to 48.4, with an average of 37.4, and the chrome leathers from 36.9 to 62.2, with an average of 51.2.

The area change for the same period is shown in Table 65 and in the form of smoothed curves in Fig. 447. The area at zero relative humidity is taken as unity and the percent increase in area with increasing relative humidity calculated from it. The extreme increase in area for the vegetable-tanned leathers varied from 4.0 to 9.4 percent, with an average of 7.0 percent, and the chrome leathers from 9.6 to 19.0 percent, with an average of 14.4 percent. The relation between water content and area change is evidently not a simple one, because the values for the two do not follow exactly the same order.

Effect of Time

When leather is transferred from an atmosphere of one relative humidity to that of another, its water content and area immediately begin to change, but it may take a long time for equilibrium to be established. Heavy leathers do not change as quickly as light ones, and the speed is also influenced by the oil content and type of finishing. Table 66 shows the area changes with time over a period of 100 days for the 18 typical shoe leathers.

Table 66. Percent by Which Area at 100 Percent Relative Humidity Exceeds That at Zero Relative Humidity after Different Periods of Time Since Leather Was Transferred from an Atmosphere of 50 Percent Relative Humidity to Atmospheres of Zero and 100 Percent Relative Humidity, Respectively.

Sample	Kind	Time in Days						
No.	of Leather	1	2	6	13	20	30	100
1.	Vegetable calf	2.0	3.2	4.4	4.9	5.5	5.7	5. <i>7</i>
2.	Chrome calf	10.4	11.5	13.4	15.8	16.0	16.0	16.4
2. 3.	Glazed kid (C)	8.8	9.6	12.8	14.9	15.6	15.6	15.6
4 . 5.	Kangaroo (C)	8.6	9.8	13.4	16.6	17.3	19.0	19.5
5.	Cordovan (V)	2.4	3.0	3.8	4.0	4.0	4.0	4.0
6.	Buck (C)	8.0	9.0	10.3	14.5	14.7	14.7	14.9
7.	Chrome side	7.5	8.6	12.8	15.1	15.3	15.8	16.9
8.	Suède (C)	7.5	8.0	10.7	13.0	13.8	13.8	14.1
9.	Calf lining (V)	5.9	6.9	7.7	9.0	9.2	9,2	9.4
10.	Sheep lining (V)	6.5	7.5	9.0	9.4	9.4	9.4	9.6
11.	Shark (V)	3.8	4.4	5.5	7.5	7.9	8.0	8.2
12.	Patent side (C)	5.7	<i>7</i> .1	9.0	9.8	10.0	10.5	11.1
13.	Patent kid (C)	4.9	6.1	8.2	9.0	9.4	9.6	10.7
14.	Patent colt (C)	7.5	8.8	11.3	12.8	12.8	13.0	13. 6
15.	Heavy chrome	5.5	8.4	12.8	15.6	16.4	16.9	18.8
16.	Chrome retan	4.4	5. <i>7</i>	9.2	10.7	11.1	11.5	12.4
17.	Vegetable sole	3.4	3.7	4.4	4.9	5.5	5.5	5.5
18.	Chrome sole	4.4	6.0	9.0	11.3	12.4	13.0	15.3

(C) indicates chrome tannage; (V) indicates vegetable tannage.

In studying these figures, it should be noted, in the ratio of the area at 100 percent relative humidity to the area at zero relative humidity, that both numerator and denominator are changing with time. If the test had been carried out with the leathers initially in equilibrium with a dry atmosphere, the change the first day would have been much greater.

An example of this is shown in Fig. 448 for a light chrome calf leather and a heavy chrome side leather, not included in the 18 leathers being studied. After 14 days the two leathers were returned to the dry atmosphere and the curves illustrate the reversibility of the process. In going from one extreme of relative

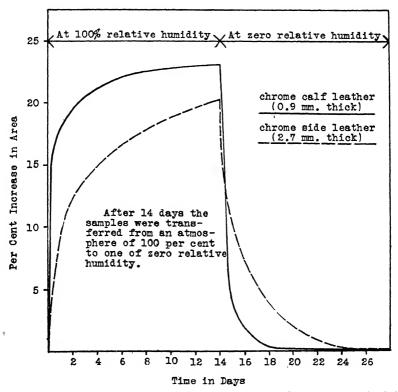


Fig. 448. Area Change of Leather with Time Following a Sudden Change in Relative Humidity of the Atmosphere from Zero to 100 Percent and Then Back Again to Zero.

humidity to the other, the change is very rapid; the chrome calf leather increased more than 11 percent in 4 hours and showed a correspondingly large decrease in area when first returned from the wet to the dry atmosphere. Thickness may explain the difference in rate of change between these two leathers, but it will not explain why the vegetable-tanned sole leather reached equilibrium in much less time than the very thin kangaroo leather.

No single factor will explain all the differences in area change found for the different leathers. At the 100-day period, the extreme area change for the vegetable-tanned leathers varied from 4.0 to 9.6 percent, with an average of 7.1 per-

cent and for the chrome leathers from 10.7 to 19.5 percent, with an average of 15.2 percent. The effect of kind of tannage is clearly very great and the one outstanding cause for big differences. The lacquered surfaces may explain why the area changes for the patent leathers are lower than for the other chrome leathers. One might be tempted to suggest that the extremely low area change of the cordovan leather was due to its high fat content were it not for the fact that the kangaroo leather also has a high fat content and yet shows the greatest area change of all. Of course it is possible that the kangaroo leather might have shown a still greater area change had its fat content been lower; several samples of chrome calf leather were examined showing area changes greater than 23 percent.

Effect of Glycerin

In an unpublished work, Wilson and Kern studied the effect of finishing materials upon the area change of leather with relative humidity and noted a marked effect when glycerin was added to the finished material. A sample of chrome calf leather was used for the tests. After 35 days at zero relative humidity, its water content was 1.79 parts per 100 of dry leather; this increased with increasing relative humidity to a value of 57.92 in water-saturated air. When 5 grams of glycerin per sq. ft. of leather was applied to the grain surface, the water content of the leather after 35 days was 4.51 parts per 100 of dry leather at zero relative humidity and 79.25 at 100-percent relative humidity. The glycerin markedly increased the affinity of the leather for water. In going from dry to moist air, the original leather increased in area by 20 percent. The effect of the glycerin was to give the leather an area at zero relative humidity 1.4 percent greater than it would otherwise have had. This increase persisted over the entire range of relative humidities. At all stages the glycerin-treated leathers had an area from 1 to 2 percent greater than the untreated leathers.

Practical Tests

Wilson and Gallun made a number of practical tests under rigidly controlled conditions. Several calfskins were cut into sides and one of each was chrome tanned and the other vegetable tanned. For each man taking part in the test, two pairs of shoes were made, one pair from the chrome-tanned side and the other from the vegetable-tanned side of the same skin. During one period, he would wear a chrome-leather shoe on the left foot and a shoe of vegetable-tanned leather on the right foot and then reverse this during another period. When the weather was damp, the chrome shoe was too big, and when the weather was very dry, it was too tight to be comfortable. This was noticeable to a very much lesser degee with the shoes of the vegetable-tanned leather. After entering a warm, very dry room when it was cold outside, the difference in shrinking and tightening of the two shoes was very marked.

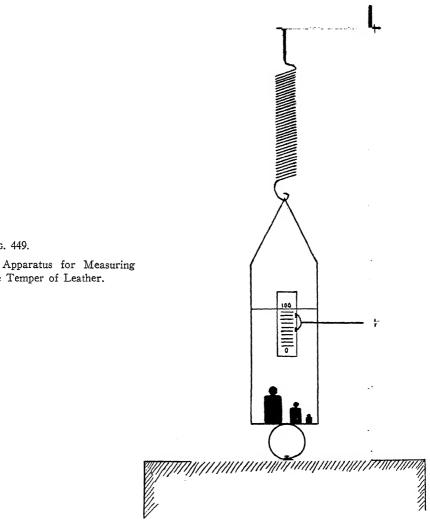
In one test, a shoe of each kind was kept for several days in an atmosphere of 100 percent relative humidity and then transferred to one of zero relative humidity. The width of the upper of the chrome shoe, measured just back of the toe cap, was found equal to a standard D-width at 100 percent relative humidity, but decreased to the equivalent of a B-width when kept for a week at zero relative humidity. The change in the shoe of vegetable-tanned leather was only about one-third as great. In some cases, the man making the test could not squeeze his foot into the chrome shoe when it had just been taken from an atmosphere of zero relative humidity.

A glance at Figs. 445 and 446 will show that the curves are flattest in the region

of 50 percent relative humidity. Where there is no great variation in relative humidity from this value, one would not expect to find much difference in the size changes between shoes made of the two kinds of leather. The greater shrinkage of the chrome leather is somewhat offset, also, by its greater ease of stretch. But where the conditions are severe, the kind of tannage becomes an important

Fig. 449.

the Temper of Leather.



factor in foot comfort. Greeves quotes an officer of long experience in the World War of 1914 and one who knew a great deal about leather, to the effect that chrome shoes were most uncomfortable to sleep in, many soldiers risking trench feet and frostbite rather than lie down in chrome shoes. It is also reported that there was always a rush on the part of soldiers who knew the difference in comfort to get vegetable-tanned shoes. Sportsmen who have made the test say that at the end of a day's tramping for shooting, the feet ache less in vegetable-tanned than in chrome shoes. The work of Wilson and Gallun received very wide newspaper publicity throughout the world as having solved the riddle of the weather prophet who foretells changes in the weather by the pain in his corns. The corns merely respond to shrinkages in the leather of the shoes.

Temper of Leather

One of the methods used by the shoe manufacturer to judge the quality of leather for shoe uppers is to fold the right side of the skin over the left, flesh side in, and then to run his hand up and down the region of the backbone, noting the pressure required to squeeze the two sides together and the vigor of rebound of the leather upon release of the pressure. The property measured in this crude way is generally known as temper, and it is recognized that temper has an influence upon both the comfort of the shoe and its appearance in actual wear.

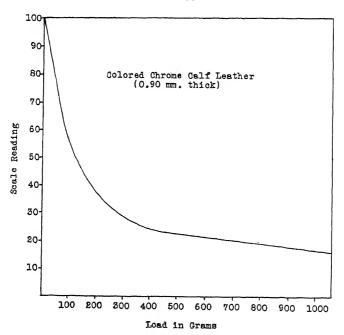


Fig. 450. Degree of Compression of a Circle of Leather as a Function of Load in the Apparatus for Measuring Temper Shown in Fig. 449.

The author has studied the property called temper and devised a method for the quantitative measurement of its two components, flexibility and recovery. The apparatus is pictured in Fig. 449. The base is a solid maple block into which is set vertically an iron rod. From an adjustable arm attached to this rod, a balance pan with flat base is suspended by means of a spiral spring of appropriate size. Attached to another adjustable arm is a scale 4 cm. long with 100 equal divisions. A fine wire to be used in reading the scale is drawn across the pan supports. The position of the scale is set to give a reading of zero when the pan rests upon the block.

The leather to be tested is cut with a die 1×6 in. Tack holes are punched near the ends of the leather 12.57 cm. apart and equidistant from the sides. The leather is drawn into a circle, grain side out, and the ends are joined by means of a thumb tack, which is inserted in the block at a point corresponding to the vertical projection of the center of the pan on the block. If the leather has a negligible thickness and forms a perfect circle, when weights enough are placed on the pan to bring it to the point where it just touches the leather, the scale reading will be 100, since the diameter of a circle with a circumference of 12.57 cm. is 4 cm., which is the length of the scale. Unfortunately, the finite and variable thickness of leather strips to be tested complicates the measurement and necessitates the establishment of arbitrary standards.

Fig. 450 shows how the scale reading varied for a strip of chrome-tanned calf leather, 0.90 mm. thick, when an increasing load was placed upon the pan. The curve resembles the familiar die-away curve of the hyperbolic type. After the diameter of the circle of leather has been reduced to less than one-quarter of its initial value, it ceases to be sensitive to small increases in pressure. Further compression tends to crease the leather in two places, pulling apart the fibers in the grain layer and crushing together those in the flesh layer. The resistance of the leather to this further compression involves more than is included in the term temper. The reading at which this extra resistance becomes apparent increases with the thickness of the strip of leather being tested.

In comparing temper values of different leathers, it seemed logical to the author to select some degree of compression that would correspond to the qualitative test made by the shoe manufacturer, that would be great enough to test the ability of the leather to recover, that would be small enough to avoid too great complication due to including the extra resistance not involved in temper, and that would compensate for variations in thickness of different leathers.

If the scale reading when the pan just rests upon the circle of leather is 100, the pan can be forced down to a point a distance above the block equal to two thicknesses of leather. One mm. equals 2.5 units on the scale. Taking t as the thickness of the leather in mm., the pan may be forced through a distance equal to 100 - 5t units on the scale. In his work, the author has selected the arbitrary value for degree of compression equal to three-quarters of this or to a scale reading of (100-5t)/4 above 5t, or an actual scale reading of 25 + 3.75t.

In making the measurement with a strip of leather in place, weights are placed upon the pan until the scale reading is 25 + 3.75t. The weight required is called W_1 . Its value depends, not only upon the flexibility of the leather, but also upon the resistance of the spiral spring. The weight required to depress the pan to give a reading of 25 + 3.75t with no leather is called W_2 . The weight required for the leather alone is thus given by the equation $W = W_1 - W_2$. This is called the flexibility factor, one of the elements making up the temper of the leather.

The other factor is the percentage recovery of the diameter of the circle of leather when the weights are released. Immediately after depressing the leather to give a reading of 25 + 3.75t, the weights are removed and then weights are again added until the pan just touches the leather and the scale reading is noted. This reading, r, enables one to calculate the percentage recovery, R, from the formula

$$R = \frac{r - 25 - 3.75t}{0.75 - 0.0375t}$$

Effect of Splitting

Two series of tests were made to show the effect of reducing the thickness of chrome-tanned calf leather by splitting. In each case only the grain split was tested. The results are shown in Fig. 451.

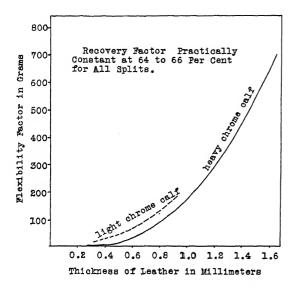


Fig. 451.

Effect of Reducing Thickness of Chrometanned Calf Leathers by Splitting upon Their Temper Values.

Splitting reduces the flexibility factor very sharply, but is without effect on the recovery factor. The flexibility factor is also reduced by staking, graining and increasing the contents of water or fat.

Typical Temper Values

Typical temper values for shoe-upper leathers are shown in Table 67.

The table shows measurements for both butt and belly regions where these were available. In most cases, the flexibility factor was much less in the belly than

mple Kind No. of Leather		Thickness		Flexibility factor (grams)		Recovery Percent	
of Leather	Butt `	Belly	Butt	Belly	Butt	Belly	
Vegetable calf	1.20	1.20	380	285	64	64	
Chrome calf	1.10	1.10	330	230	72	61	
Glazed kid	0.82	0.74	113	7 8	65	65	
Kangaroo	0.59	0.53	63	10	70	45	
Cordovan	1.15		435		69		
Buck	0.88	0.85	100	37	80	72	
Chrome side	1.30	1.20	400	130	5 <i>7</i>	49	
Suède	0.70	0.95	13	14	63	58	
Calf lining	0.82	0.75	285	150	67	62	
Sheep lining	0.97	0.70	125	138	67	58	
Shark	0.80	0.85	175	95	64	64	
Patent side	1.08	1.00	135	32	60	48	
Patent kid	0.94	1.06	68	52	65	65	
Patent colt	1.48	1.35	300	175	5 <i>7</i>	66	
Heavy chrome	2.70		1200		65		
Chrome retan	2.65	2.60	950	950	54	54	
	of Leather Vegetable calf Chrome calf Glazed kid Kangaroo Cordovan Buck Chrome side Suède Calf lining Sheep lining Shark Patent side Patent kid Patent colt Heavy chrome	Kind of Leather Rutt Vegetable calf 1.20 Chrome calf 1.10 Glazed kid 0.82 Kangaroo 0.59 Cordovan 1.15 Buck 0.88 Chrome side 1.30 Suède 0.70 Calf lining 0.82 Sheep lining 0.97 Shark 0.80 Patent side 1.08 Patent kid 0.94 Patent colt 1.48 Heavy chrome 2.70	Kind of Leather (mm.) Vegetable calf 1.20 1.20 Chrome calf 1.10 1.10 Glazed kid 0.82 0.74 Kangaroo 0.59 0.53 Cordovan 1.15 Buck 0.88 0.85 Chrome side 1.30 1.20 Suède 0.70 0.95 Calf lining 0.82 0.75 Sheep lining 0.97 0.70 Shark 0.80 0.85 Patent side 1.08 1.00 Patent kid 0.94 1.06 Patent colt 1.48 1.35 Heavy chrome 2.70	Kind of Leather Butt (mm.) Belly factor (Butt) Vegetable calf 1.20 1.20 380 Chrome calf 1.10 1.10 330 Glazed kid 0.82 0.74 113 Kangaroo 0.59 0.53 63 Cordovan 1.15 435 Buck 0.88 0.85 100 Chrome side 1.30 1.20 400 Suède 0.70 0.95 13 Calf lining 0.82 0.75 285 Sheep lining 0.97 0.70 125 Shark 0.80 0.85 175 Patent side 1.08 1.00 135 Patent kid 0.94 1.06 68 Patent colt 1.48 1.35 300 Heavy chrome 2.70 1200	Kind of Leather (mm.) factor (grams) Butt Belly Butt Belly Vegetable calf 1.20 1.20 380 285 Chrome calf 1.10 1.10 330 230 Glazed kid 0.82 0.74 113 78 Kangaroo 0.59 0.53 63 10 Cordovan 1.15 435 Buck 0.88 0.85 100 37 Chrome side 1.30 1.20 400 130 Suède 0.70 0.95 13 14 Calf lining 0.82 0.75 285 150 Sheep lining 0.97 0.70 125 138 Shark 0.80 0.85 175 95 Patent side 1.08 1.00 135 32 Patent colt 1.48 1.35 300 175 Heavy chrome 2.70 1200	Kind of Leather Butt Melly Butt Butt Belly Butt Ge 64 Chrome calf 1.10 1.10 330 230 72 72 Glazed kid 0.82 0.74 113 78 65 78 Kangaroo 0.59 0.53 63 10 70<	

Table 67. Temper Values for Typical Shoe-upper Leathers.

in the butt, which is in accord with the looser structure of the belly portions. The author was surprised not to find a greater variation in the percent recovery. The very low flexibility factors for kangaroo, kid and suède are what one would expect from their behavior in wear.

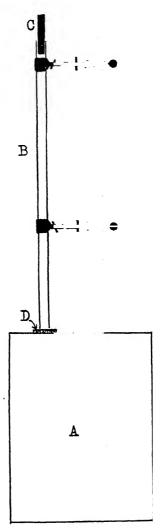


Fig. 452.

Apparatus for Measuring the Resilience of Leather. A: solid maple block. B: calibrated glass tube. C: brass plunger. D: leather sample.

Resilience of Leather

Resilience is a property of leather closely associated with temper and is particularly important in sole leather, which does not lend itself to temper measurements. The very simple apparatus designed by the writer for measuring the resilience of leather is shown in Fig. 452.

It may be found convenient to use the same block and supporting rod as that used in the apparatus for measuring temper. In the laboratory, the calibrated

glass tube may conveniently be made from an old burette with calibration marks already on it. Otherwise the distance from the point from which the bottom of the plunger is to be dropped to the leather surface must be marked on the glass tubing and divided into 100 equal parts and numbered from the top down. In making the test, the bottom of the plunger is held exactly at the 100-mark and then released. It falls, striking the leather, and then rebounds. The highest point reached by the bottom of the plunger in the rebound represents the percentage rebound.

In the writer's work, the plunger weighed 1.712 oz. and had a diameter of § in. The 100-mark on the tube was 23§ in. above the leather surface. The plunger does a certain amount of work in compressing the leather when it falls upon it and the leather then returns a certain fraction of the energy it has received, measured by the percentage rebound of the plunger, which thus becomes a measure of the resilience of the leather.

If the leather were immeasurably thin, the value found for resilience would be merely that of the maple block. In order to get the resilience of the leather itself, it was found necessary to have a thickness of leather of at least 3 mm., or about $7\frac{1}{2}$ oz. When thinner leathers are to be tested, it is necessary to pile up two or more disks of the leather to make a total thickness of about 3 mm. For heavier leathers, no such precautions need be taken.

Resilience of Typical Leathers

Typical resilience values of various leathers are shown in Table 68. All samples were in equilibrium with an atmosphere of 50 percent relative humidity, and disks were built up to a minimum thickness of 3·mm. where necessary. This required 6 thicknesses for the very thin kangaroo leather.

Table 68. Resilience of Various Leathers in Terms of the Percentage Rebound of a Plunger Dropped upon Them Under Certain Prescribed Conditions.

_		_	
	Sample No.	Kind of Leather	Resilience
	1.	Vegetable calf	22
	2.	Chrome calf	26
	3.	Glazed kid	2 8
	4.	Kangaroo	24
	5.	Cordovan	16
	6.	Buck	23
	7.	Chrome side	21
	8.	Suède	21
	9.	Calf lining	22
	10.	Sheep lining	21
	11.	Shark	23
	12.	Patent side	19
	13.	Patent kid	22
	14.	Patent colt	23
	15.	Heavy chrome	17
	16.	Chrome retan	11
	1 7.	Vegetable sole	39
	18.	Chrome sole	17
	x	Rubber heel	20

Effect of Water and Grease

Because the resilience of the chrome-tanned sole leather was so much lower than that of the vegetable-tanned sole leather, it was suspected that this might be caused by its high grease content. A sample of the chrome-tanned sole leather was

degreased and tested again, whereupon it was found that the resilience had jumped from 17 to 34.

Although vegetable-tanned sole leather contains relatively little grease, tests were run to show the effect of water content on the resilience of both degreased and undergreased leather. Fig. 453 shows the water contents of both degreased and undegreased leathers in equilibrium with atmospheres of different relative humidities. Degreasing the leather caused it to take up more water at any relative humidity. Fig. 454 shows the effect upon resilience. With increasing relative humidity

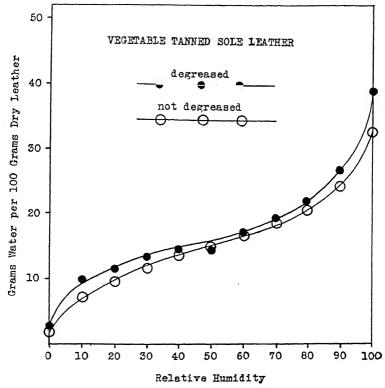


Fig. 453. Water Content of Vegetable-tanned Sole Leather as a Function of Relative Humidity of the Atmosphere.

and water content, the resilience of both degreased and undegreased leather falls, but the resilience of the undegreased leather is less at all relative humidities than that of the degreased leather.

Wear Resistance of Leather

Most of the work on the resistance of leather to wear has been done on sole leather, which is natural in view of the fact that practically all the really hard wear of a shoe occurs on the heels and soles. Shoe uppers receive relatively little damage through wear, making it possible to sacrifice wear resistance to some extent where this is necessary to gain something in other properties.

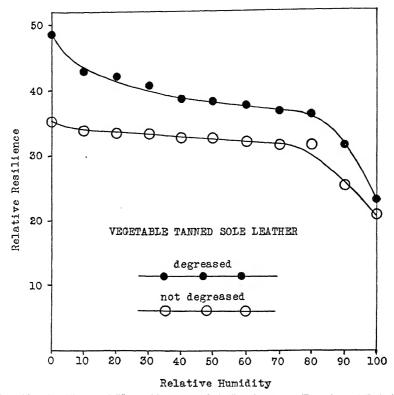


Fig. 454. Resilience of Vegetable-tanned Sole Leather as a Function of Relative Humidity of the Atmosphere.

Bowker and Geib made a very interesting study of the relative durability of soles made from chrome- and vegetable-tanned steer and buffalo hides. Comparisons were also made with chrome-tanned steer hides filled with greases and

Table 69. Chemical Compositions of Sole Leathers Tested. (percentage on dry basis)

	Seri	es 1	Serie	es 2	Seri	es 3	Ser	ies 4	Ser	ies 5	Ser	ies 6
Constituent	Filled Chrome	Vegetable	Natural Chrome	Vegetable	Filled Chrome	Vegetable	Filled Chrome	Vegetable	Natural Chrome	Filled Chrome	Natural Chrome	Filled Chrome
Water-solubles Hide substance Grease* Insoluble ash	15.18 34.75 22.83 19.47	25.91 41.25 2.27 .15	5.85 74.20 2.73 7.90	29.85 38.36 2.41 .20	12.98 34.61 22.71	28.45 39.51 3.24 .50	(1)	31.88 37.67 3.46 .42	4.64 80.55 1.79	23.12	1.68 88.15 1.00 6.73	1.60 64.35 24.07 6.04
Combined tannin. Degree of tannage Glucose	6.03	30.43 74.00 3.64		29.18 76.00 7.18	5.54	28.30 72.00 3.80		26.57 71.00 4.66				
Epsom salts Acidity† Total ash Cr ₂ O ₃ (fat free)	20.18 5.08	.50 .42	9.87 7.22	2.17 .27 .99	23.19 4.06	3.42 2.76		.30 2.80	8.00 5.24		6.75 5.55	6.08 6.23

¹ Same as leather used in series 5.

^{*} Petroleum ether extract.

[†] Procter-Searle method.

mineral fillers. The different types of soles were paired off, a man wearing one kind on the left foot and the other on the right. The pairs of test soles were attached to men's shoes and worn by laboratory workers, office workers, electricians, plumbers, machinists, firemen, and outside laborers. In cases where the vegetable sole wore out first and there was sufficient wear left in the chrome sole to warrant it, another vegetable sole was attached in order to secure the actual time under service conditions required for the chrome sole to wear through. In cases where this procedure was not feasible and a sole was not worn completely through, the thickness worn away was determined and the total probable length of wear was calculated.

Table 69 gives the chemical compositions of the leathers used in the tests and Table 70 gives the results of the wear tests.

				2 0000 011	DOIG LOUGHE	•	
Series No.	Description of Leather	Number of Soles Tested	Average Iron per Sole	Days Wear per Sole	. Days Wear per Iron	Longer W Chrome L Filled	
						Percent	Percent
1	Filled chrome	28	8.0	80.8	10.1	23.2	
1	Vegetable	28	8.1	66.4	8.2		25.5.5.2
2	Natural chrome	33	8.0	192.1	23.9		111.5
2	Vegetable	33	9.9	111.5	11.3		••••
3	Filled chrome	140	8.2	131.2	16.0	40.3	
3	Vegetable	140	8.1	92.2	11.4		
4	Filled chrome	63	9.4	195.0	20.9	115.5	• • • •
4	Vegetable	63	8.7	84.3	9.7		• • • •
7	vegetable	0.5	0.7	07.5	3.7	• • • •	• • • •
5	Natural chrome	76	7.2	210.0	28.5		20.5
5	Filled chrome	76	7.4	175.4	23.7		
6	Natural chrome	88	10.5	350.2	33.2		10.7
ő	Filled chrome	88	11.1	333.9	30.0		
-							

Table 70. Results of Wear Tests on Sole Leather.

To the layman, the use of the term *iron* in Table 70 may be confusing without an explanation. The thickness of sole leather is usually measured in terms of *irons*; an iron is simply $\frac{1}{48}$ inch. Where the average iron per sole was 8.0, it simply means that the average thickness was 8.0/48 or $\frac{1}{6}$ inch.

A summary of the results of the weekly inspections and the comments of the individual wearers led to certain general conclusions regarding the behavior of the chrome sole leather in actual service. The natural chrome leathers became very soft and pliable; had a decided tendency to spread and curl up on the edges; allowed water to penetrate rapidly; frayed on the edges, thus detracting from the shoe's appearance; and slipped readily on smooth, wet objects. The leather filled with paraffin, although very hard when first put on the shoe, soon became pliable, spread, frayed some on the edges, slipped, and after a certain period of wear seemed to loose its water-resistant property, due probably to the working out of the hard paraffin wax by flexing. The leather filled with paraffin and pyroxylin acted in like manner, excepting that it did not fray to such an extent and seemed to retain its water-resistant property longer. Of all the filled leathers, that used in series 1 and 3, which had considerable mineral material added, was superior in all the above-mentioned characteristics and appeared to remain as firm and water-resistant throughout as the vegetable leather.

^{* 48} irons=1 inch.

As a result of their investigation, Bowker and Geib formulated the following conclusions:

1. Natural and paraffin-filled chrome sole leather will wear approximately twice as

long as vegetable sole leather per unit of thickness.

2. Natural chrome will give the longest wear, paraffin-filled ranking next, and that additionally filled with mineral material ranking third, the latter, however, wearing about

one-third longer than vegetable.

3. Although vastly superior in wearing quality by comparison with the vegetable leather, chrome sole leathers, in general, have disadvantages in appearance, lack of firmness, lack of water resistance, and tendency to slip which can be only partly overcome by the addition of certain filling materials. Whereas such chrome leathers have a limited application, the field of usefulness could be broadened with consequent economic advantage to the public by reason of the greater wear obtainable, should a method of preparing chrome leather be developed which would give it more nearly the desirable qualities of the vegetable leathers.

Veitch, Frey and Clarke had previously noted this greater durability of chrometanned sole leather. They also found that soles cut from the butt of the hide wore longer than soles cut from the shoulder, and that rolled leathers wore longer than leathers not rolled. Bowker observed that the life of a sole can be increased by increasing its grease content and flexibility.

The effect of filling or loading materials has received some study. Wormeley, Bowker, Hart and Whitmore found that loading sole leather with glucose and Epsom salts had practically no effect upon its wearing quality; these materials are soon leached out of the leather when walking on wet pavements. Bowker showed that filling sole leather with sulfite cellulose extract gave a leather as durable as one filled with ordinary tanning extracts, such as quebracho or chestnut wood.

Hart studied wear resistance at different depths in the hide. Eighteen test pieces were prepared from one vegetable-tanned hide and divided into six groups, three of which were tested by wearing with the grain side out and three by subjecting the flesh side to the wearing action. Of the three tested with the grain side out, the first was left with its original thickness, the second was made approximately two-thirds of its original thickness by skiving off one-third from the grain surface, the third was reduced to one-third of the original thickness by skiving off two-thirds from the grain side. A similar comparison was made with the three pieces worn flesh side out. The testing was done on a laboratory wear-test machine. The greatest resistance to wear occurred in the middle of the hide, which wore twice as long as the outer grain or flesh layers.

Measurements of wear resistance or resistance to abrasion are very important to all tanners because they can be varied by appropriate treatments of the leather. The writer devised an apparatus for measuring wear resistance that is so simple that any tanner can have one made in his own machine shop and it is very inexpensive. Most young boys, at one time or another, like to build workshops and do carpentry work. Various hardware stores specialize in equipment for such workshops and one readily available item is an electric sanding machine for sanding woodwork. This usually costs only a few dollars, but with one a tanner can make a very satisfactory machine for measuring wear resistance of leather.

Two of the writer's wear-testing machines are shown in Fig. 455. Each is built from a toy sanding machine. The sanding machine as purchased is equipped with an endless belt of Carborundum paper, which travels at the rate of 176 linear feet per minute. The part that the tanner must have built for himself is that shown above the belt. It consists of a brass plate to which is attached two brass legs with removable feet equipped to hold squares of leather 1 square inch in area. The pieces of leather rest on the moving Carborundum belt. A cam device is provided to raise and lower the feet alternately so that the leather rests on the belt just 40 percent of the time. This is sufficient to dissipate the frictional heat developed so that the leather does not warm up appreciably during the tests. The weight of each brass leg and foot together is 4.6 oz. so that the leather rests on the belt under a pressure of 4.6 oz. plus the weight of the leather.

In making a test, 1 square inch of leather is set into the brass foot after measuring its thickness in inches accurately with a Randall & Stickney gauge like that shown in Fig. 202 of Chapter 11. The thickness can be measured accurately

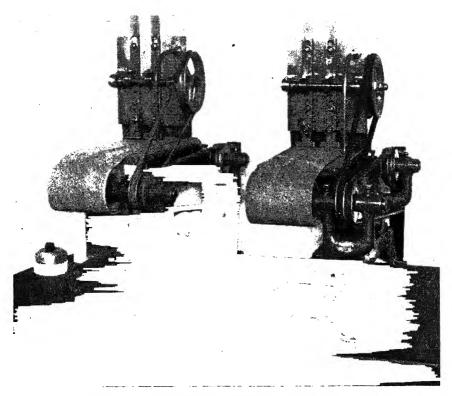


Fig. 455. Apparatus for Determining the Relative Wear Resistance of Leather.

to 0.001 inch. The machine is then run for exactly 9 hours and the thickness of the leather is measured again. The difference in thickness between the first and second measurement is the loss in thickness of the leather in inches. To get the wear resistance of the leather, it is now necessary merely to divide 1.0 by the loss in thickness of the leather after running 9 hours.

For leathers that are too thin to be inserted in the brass foot, it has been found satisfactory to cement them to wooden squares about & inch thick and then to measure the thickness of both wood and leather, since it is necessary only to learn the loss in thickness of the leather in inches.

Although the measurement is really one of resistance to abrasion, thousands

of tests have shown that it furnishes a fairly reliable guide as to the durability of leathers that must be subjected to frictional wear. Determinations can be made with the expenditure of very little time and effort. Determinations of the effect of changes in tannery operations upon the wear-resistance values have proved very valuable in developing leathers of high durability both for heavy and for light leathers. Table 71 gives a few typical results obtained by this method.

Table 71. Wear Resistance Values Obtained on Various Leathers.

	Wear
Kind of leather	resistance
Vegetable-tanned sole leather of poor wearing qualities	. 13
Vegetable-tanned sole leather of good wearing qualities	
Chrome-tanned sole leather (steer hide)	. 117
Chrome-retanned sole leather (steer hide)	. 56
Chrome-retanned sole leather (horse butt)	
Football leather (vegetable-tanned steer)	
Calf (vegetable tanned)	
Calf (Calgon-tanned, vegetable-retanned)	
Kid (vegetable-tanned)	
Baseball (alum-tanned horse)	
Baseball (Calgon-tanned, alum-retanned horse)	
Baseball (Calgon-tanned horse)	

Wear resistance is greater for chrome-tanned leathers than for vegetabletanned leathers and is greater for Calgon-tanned leathers than for chrome-tanned leathers. It is increased by increasing fat content.

Firmness of Heavy Leathers

Another property, particularly important in sole leather, is that of firmness. This property is to heavy leather what temper is to light leather. Like it, it has both a flexibility factor and a recovery factor. A simple instrument devised by the writer for measuring the firmness of leather is shown in Fig. 456. Relative firmness is defined as the number of lbs. pull required to bend a strip of leather 1 in. wide to a radius of curvature of the grain surface of 1.45 in., with chord of the arc 2 in.

Fig. 456 shows the two jaws of a Scott vertical tensile-strength machine, which is equipped with a recording device for measuring percent stretch. upper jaw is clamped a device made of two heavy plates of brass soldered together. In the lower plate, there is a slot one inch wide. Into the lower jaw is clamped a device made of three heavy plates of brass soldered together. Each of the upper two plates has a slot one inch wide and the two slotted plates are parallel and spaced exactly two inches apart. A strip of leather 1 by 6 in. is placed so that it passes through all three slots, grain side up, and the slots are so spaced that the grain side of the leather just touches the upper edges of the two lower slots, and the flesh side just touches the lower edge of the upper slot with the leather lying in a horizontal plane. With the stretch-recording device set for a distance between the jaws of 4 in., the machine is run until the recorder indicates a stretch of 10 percent. At this point, the load in lbs. is recorded as the measure of relative firmness. At this point also, the plunger of the machine to return the load to zero is pushed and the reading is taken at which the load just reaches zero and from this reading the percentage recovery can be calculated. For example, if the reading returns from the 10 percent to the 2 percent stretch line at zero load, the recovery is 80 percent.

A few typical values for relative firmness of sole leathers are as follows: finders' bend 65, manufacturers' leather 30, flexible sole leather 10, chrome sole 20, chrome-retan sole 11 and chrome-retan horse butt 5. The relative firmness varies with thickness, location, pressure of rolling, oil content, etc. With this method, it has been possible to develop degrees of firmness desired by noting the effects of various treatments in the tannery upon the measurements of relative firmness.

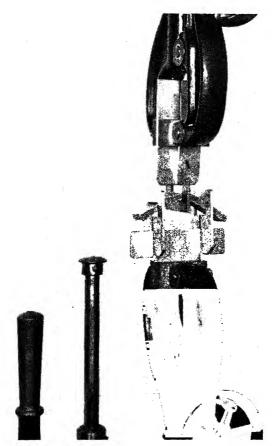


Fig. 456. Apparatus for Measuring Relative Firmness of Sole Leather Set in Jaws of Vertical Tensile Strength Machine.

Resistance of the Grain of Leather to Cracking

If the grain surface of leather will not resist cracking in service, its value becomes very low. Table 60 gives the precent stretch at which the grain layer cracked during the stretching of a great variety of satisfactory leathers. In many cases, the grain did not crack until the leather broke. The danger of cracky grain in the case of sole leather increases when the leather is heavily loaded with sugar and some other materials. In the determination of relative firmness of sole leather just described, the grain surface should not crack. If it does, the point at which

cracking occurs should be noted and steps should be taken in the manufacture, such as washing or cutting down the load of sugar until no cracking occurs during the test on the finished leather. Any sole leather cracking under the conditions of this test should be looked upon with suspicion.

Resistance of Leather to Hot Water

When dry, most leathers will stand temperatures exceeding 212° F. without appreciable harm, but, when wet, they show degrees of resistance to heat depending upon the kind and degree of tannage. Chrome or quinone-tanned leathers will withstand the action of boiling water and very heavily tanned chrome leathers will even withstand the action of steam under pressure. Vegetable-tanned leathers are destroyed by water at a temperature much over 158° F. and oil-tanned leathers at temperatures much over 140° F. Ordinarily, the temperature of destruction of wet leather has only a theoretical significance, always being much greater than the human body can stand, but it becomes of considerable practical importance when one attempts to dry wet leather more quickly by the application of heat. Many a sole has been ruined by placing a wet shoe on a steam coil or close to a fire. Leather should always be dried slowly and it may be kept soft and pliable by rubbing a little olive oil over the grain surface while the leather is still wet. This is good practice after cleaning leather with soap and water, which is, by the way, the best method of cleaning it.

Effect upon Lasting in Shoe Making

The lesser resistance of vegetable-tanned leather to hot water has led some shoe manufacturers to prefer chrome-tanned upper leather because less attention must be paid to temperature in mulling or conditioning the leather before lasting. This is regrettable because the ultimate consumer is denied the superior advantages of the vegetable-tanned leather for an advantage to the shoe manufacturer that is of questionable value. In a private communication to the author, Mr. F. W. Eagan of the Beckwith Manufacturing Company of Boston has discussed the problem of lasting chrome and vegetable-tanned leathers in a very clear manner. Almost all lasting rooms are now fitted with hot-vapor heaters to assist in lasting the toe of the shoe smoothly. Heat and moisture are applied to the grain surface of the leather to bring it to a properly mulled and softened condition before lasting. All upper leathers will yield to this treatment, if properly handled, without injury, although some tannages will stand more heat and vapor than others.

If the shoe manufacturer has had no experience with the lasting of vegetable-tanned upper leathers, it is well first to experiment with small pieces of the leather to find just the right temperature and volume of vapor to be used before inserting the shoe. All vegetable-tanned leathers may be mulled satisfactorily, if the heater is properly regulated. Vegetable-tanned upper leathers yield nicely to a lower temperature and lesser volume of vapor by exposing for a longer period of time and this can be done without any danger of damaging the leather or of discoloring the finish. For example, exposure for 4 minutes at 150° F. will produce the desired mulling effect without any injury to leather or finish, whereas the same piece of leather would be spoiled by a one-minute exposure at 215° F. for more.

Toe heaters should be so arranged that the temperature and volume of vapor can be controlled separately and no condensed water should be allowed to fall upon the toe of the shoe or discoloration may result. The cut edges of the leather should be watched; if they start to curl, it is a sign that the volume of hot vapor applied is too great.

Ability of Leather to Retain Embossing

Leathers are often embossed, tooled, or stenciled for various purposes and then it is important that the design be retained as nearly permanently as possible. In this both the structure of the skin and the kind of tannage play a very great part. A very full and tight structure is required; calfskin gives the ideal structure for the finer leathers and cowhide for the coarser. The vegetable tannage is far superior to the chrome because it builds up the fibers to a much greater extent and makes the structure correspondingly tighter. Vegetable-tanned calf leathers are used very extensively for the finer grades of tooling leathers.

The Break of Leather

In judging the value of leather for very fine shoe uppers or for very fine novelties, much importance is attached to the fineness of what is called the "break" of the leather. What is meant by the break of leather will be made clear by a description of the author's method of measuring it. A strip of the leather, grain side in, is drawn tightly about a glass rod 3.2 mm. in diameter so that the edge of the leather is just flush with one end of the rod. A line is drawn across the end of the rod through its center. It will be noted that the grain becomes puckered or wrinkled and the number of wrinkles over half of the circumference may be counted from one end of the line to the other. This number multiplied by two gives the number of wrinkles per centimeter. This is a quantitative measure of the break of the leather, the greater the number of wrinkles per centimeter, the finer the break. A leather with 25 or more wrinkles per centimeter is said to have a fine break; one with 12 a fair break; and one with 6 a coarse break.

Usually the break is measured only in a qualitative way by pressing on the grain of the leather with the pointer of the right hand and drawing up the leather around it with the fingers of the left hand. The break is greatly influenced by the amount of oil in the grain layer increasing in fineness with increasing quantity of oil. The butt of a skin usually has a finer break than the shoulder and the shoulder a finer break than the belly. Calfskins have much finer breaks than cowhides and cowhides finer breaks than some kid skins. Tighter skins have finer breaks than looser ones. Improper methods of finishing may make an otherwise fine break very coarse. The kind of tannage has but little effect upon the break. Obviously the test is only applied to light leathers and involves cowhides only when split down to be used for light shoe uppers.

Color and Warmth

Wilson and Diener made a study to determine how much the color of the leather has to do with the heat developed when a shoe is exposed to sunlight. On a clear summer's day, if one keeps one's foot in the sunlight very long, it will get uncomfortably hot. If, now, a black shoe is put on one foot and a light-colored one on the other, a big difference in temperature will be felt, the foot housed in the black shoe feeling much the hotter.

Certain materials appear black only because they do not reflect light, but convert it into heat. White light contains all colors and the lighter in shade any material is, the more colors of white light it reflects and the less it converts into heat. Few people seem to appreciate how great is the difference in temperature rise between black and light-colored leathers when placed in direct sunlight. Wilson and Diener measured the difference for 8 samples of vegetable-tanned calf leathers. In each test, the bulb of a standard laboratory thermometer was covered with a single thickness of leather and all were put in the sunlight at the

same time. In only a few minutes the temperature rose to values considerably higher than the air temperature of 60° F., but to a different degree for each color of leather. The values given in Table 72 are typical of the results.

Table 72. Temperature of Leathers of Different Color in Sunlight.

	Temperature in Sunlight		Temperature
Color of leather	(°F.)	Color of leather	(°F.)
Light straw	100	Medium tan	
Sandy	102	Dark tan	. 110
Very light tan		Very dark tan	
Light tan		Black	. 116

The black leather actually registered 16 degrees warmer than the light straw-colored leather in direct sunlight. The temperatures were reached in a few moments and did not go any higher. In repeated tests, the actual values obtained varied, but the relative order was maintained. The amount of mist in the air, velocity of wind, moisture in the leather, and kind of tannage affect only the absolute values; the relative values depend upon color. Values obtained with chrome leather were essentially the same as those with vegetable-tanned leathers. The results show the advantage of wearing light-colored shoes during the day in summer and black shoes in winter.

Resistance of Leather to Acids

Specimens of vegetable-tanned leathers thousands of years old have been found in a remarkably fine state of preservation. On the other hand, certain vegetable-tanned leathers used in bookbindings have had a relatively short life. For nearly a century this deterioration of certain bookbinding leathers has received much attention and study. Analyses of the deteriorated leathers always showed the presence of sulfuric acid and the destruction was usually greatest and occurred in the shortest time where the highest proportions of acid were present in the leather. This resulted in an effort to make vegetable-tanned leathers in such a way that all contact of skin or leather with sulfuric acid during the processes of manufacture would be avoided, but it was found that some leathers, originally free from acid, acquired it from polluted atmospheres.

Among the important studies of the deterioration of bookbinding leathers is that of Veitch, Frey and Leinbach, who examined a number of deteriorated bindings from various public and governmental libraries. They found that leather in different sections of a deteriorated binding showed marked differences in physical condition and in chemical composition. Usually the leather in the part of the binding most exposed to air and light was most deteriorated and had the highest content of sulfuric acid as well as the greatest modification of leather substance into water-soluble nitrogen compounds.

Action of Sulfuric and Hydrochloric Acids on Calf Leathers

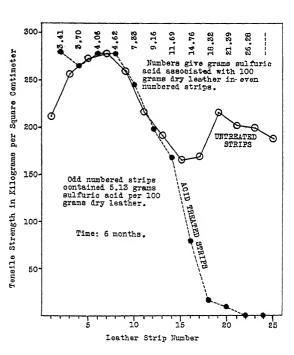
In determining the effect of the action of sulfuric acid on the strength of a piece of leather, it is necessary to know the strength both before and after the action of the acid. Obviously, the same piece of leather cannot be tested for strength both before and after an acid treatment, and so the writer developed a method for determining the strength of a piece of leather from the average strength of the pieces immediately adjoining it. In Fig. 426, curves are given showing the variation of strength of a calfskin along a line from head to tail. In the curves for

"left middle" and "right middle," if only every other strip had been tested, the strengths of the strips not tested could have been estimated approximately from the curves. This would have made available nearly one-half of the strips to be tested after special treatment.

The writer cut 25 successive strips, each 1 by 6 in., from the "right middle" of a finished chrome-tanned calfskin and numbered them successively, from head to tail, 1 to 25, inclusive. He then determined the tensile strength of all the odd-numbered strips under standard conditions and plotted the curve in Fig. 457 labelled "UNTREATED STRIPS." It was assumed that the values for the tensile strengths of the even-numbered strips lay on this line in their appropriate places. The even-numbered strips were then dipped into solutions of sulfuric acid or sodium

Fig. 457.

Illustrating Method Employed to Measure Extent of Destruction of Chrome-tanned Calf Leather by Sulfuric Acid.



bicarbonate in order to get a series of strips of different percentages of acid. These strips were blotted, air-dried and then kept for 6 months to age. Then their tensile strengths were determined under standard conditions and the results were plotted in Fig. 457 and labelled "ACID-TREATED STRIPS." The broken strips were then analyzed for water and sulfuric acid and the acid content of each strip was marked on the chart over its corresponding point.

Up to an acid content of about 10 percent the two curves practically coincide, but they diverge sharply with further increase in acid content, the acid-treated strips finally losing all measurable strength. The distance between the two curves gives a measure of the progressive loss of strength with increasing percentage of acid in the leather. For example, take strip No. 16 with a tensile strength of 79. A line drawn directly upward to the upper curve intersects it at the value 168, which may be taken as the strength of No. 16 before the acid treatment and aging. We may

therefore conclude that the treatment has caused the leather to suffer a loss of 53 percent in strength. This procedure enables one to determine the percentage loss in strength of leather resulting from any special treatment. In each test, the acid content of the leather was determined in the strip used for measuring the tensile strength.

From results obtained in this way on both chrome-tanned and vegetable-tanned calf leathers, the curves shown in Fig. 458 were drawn.

For low acid values, the acid-treated strips showed sometimes a gain and sometimes a loss whose absolute value varied from zero to 20 percent of the calculated strength of the leather, indicating that observed values below 20 percent were unreliable for this particular experiment. Hence, only the values greater than 20 percent were plotted to give the curves shown in Fig. 458. They indicate a

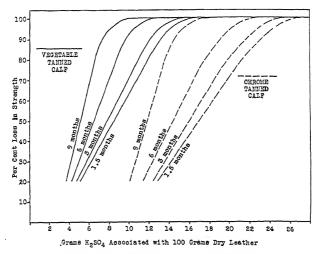


Fig. 458. Destruction of Chrome-tanned and Vegetable-tanned Calf Leathers as a Function of Aging Time and Percentage of Sulfuric Acid (H2SO4) Associated with the Leather.

progressive destruction of leather both with increasing acid content and with time. They show that acid contents greater than 4 percent for vegetable-tanned leather and 10 percent for chrome leather, as determined by the method of analysis described, will cause marked destruction of leather.

The figures do not indicate the maximum proportion of acid which the leathers may contain without danger of deterioration with time. However, the writer was fortunate in securing two vegetable-tanned calfskins tanned in the same way and having the same composition as the leather being tested, one of which was 13 and the other 20 years old. The former contained 0.60 and the latter 0.53 gram of sulfuric acid per 100 grams of dry leather. Tests made of corresponding parts of the butts of these skins and also skins recently tanned and finished by the same method showed that all had practically the same tensile strength, about 400 kg. per sq. cm. cross-section. For vegetable-tanned leather the maximum acid value that may be considered harmless would seem to lie between 0.6 and 4 percent. The experimental results given in Fig. 458 were later augmented by more, giving the results after 1 and after 2 years, but they showed no measurable change from the

results at 9 months. An acid content of 2.5 percent produced no measurable destruction of the vegetable-tanned leather in two years. The author believes that this figure must be rather close to the maximum possible without some destruction.

Effect of Concentration of Acid

The curves in Fig. 458 show that chrome leather has a greater capacity for holding acid, combined or uncombined, without causing destruction than has vegetable-tanned leather. However, chrome leather normally contains a large percentage of acid held in chemical combination, against practically none for vegetable-tanned leather. Furthermore, when the acid enters into chemical combination with leather, it actually ceases to be sulfuric acid, even though so indicated by the method of analysis employed. Most of the sulfuric acid found in chrome leather is probably present in chemical combination with the chromium. It is probably only the free acid in the leather that causes destruction.

In order to show the effect of concentration of free acid, the author kept test pieces of both kinds of leather under acid solutions of various concentrations, and the rather surprising fact was revealed that the chrome leather was much more sensitive to destruction by a given concentration of acid than vegetable-tanned leather. In fact, the tests suggested a novel method for preparing very thin sheets of leather. The surface of chrome-tanned leather is usually given a light vegetable retanning before coloring to act as a mordant. When a strip of the chrome leather 1.1 mm. thick was immersed in 6N sulfuric acid, the interior containing no vegetable tannin was dissolved away in the course of a few days, leaving behind two strips which appeared to be in perfect condition after washing and drying: a grain strip 0.1 mm. thick and a flesh strip 0.2 mm. thick, corresponding to the depth of penetration of the vegetable retannage.

The term "6N sulfuric acid" refers to a solution having a *normality* of sulfuric acid of 6. A solution of sulfuric acid with a normality of 1 contains 49 grams of pure sulfuric acid per liter, or 0.408 lb. per gal. A solution of 6N sulfuric acid contains just 6 times as much, or 2.448 lbs. per gal.

In order to simplify the experiment, the chrome leather selected for these tests was not given a vegetable retannage nor was it colored, but it was fatliquored and worked to give it the required suppleness and strength. Strips of this leather and of the vegetable-tanned leather were kept under sulfuric acid solutions of strength ranging from 0.25 to 12.00N. The containers were submerged in a constant-temperature bath at $25^{\circ} \pm 0.01^{\circ}$ C. and kept for 46 days. Then the strips were washed in running water for 48 hours and thus freed from the added acid. Analyses were made of all strips after the tensile strength measurements to make sure that any weakening of the leather was not due to acid not removed in washing. All strips of vegetable-tanned leather were found to be free from sulfuric acid and all chrome-tanned strips contained less sulfuric acid than that present in the original, untreated sample.

At the end of the 46 days the vegetable-tanned strips in the 10- and 12N acid solutions had broken into several pieces, but all the others appeared intact to the eye. But all of the chrome-tanned strips in the solutions 0.4N or stronger were dissolved or completely disintegrated. Fig. 459 shows the loss in tensile strength of the strips which had not disintegrated. In 0.2N acid, the chrome-leather suffered a loss of 83 percent in strength whereas the vegetable-tanned leather was not measurably weakened. These experiments show that the large percentage of acid normally found by analysis in chrome leather is not present as free acid; on the contrary, the great sensitivity of chrome leather to destruction by acid indicates that

only a very small amount of the acid of chrome leather is present in the free state.

The apparently much lower capacity of vegetable-tanned leather for acid seems to be due to the tannins combining with the protein groups which are otherwise capable of combining with acid and to the fact that the combined tannins lack the power possessed by the chromium nucleus to bind sulfuric acid.

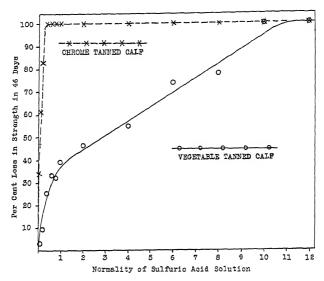


Fig. 459. Destruction of Chrome-tanned and Vegetable-tanned Calf Leathers by Contact with Solutions of Sulfuric Acid of Different Concentrations.

Action of Hydrochloric Acid

A solution of hydrochloric acid with a normality of 1 contains 36½ grams of absolute hydrochloric acid per liter, or 0.304 lb. per gal. Although sulfuric acid and hydrochloric acid differ in weight, a gallon of either having a normality of 1 contains the same number of acid hydrogen ions.

Series of strips of the vegetable-tanned calf leather were treated with hydrochloric acid solutions ranging in strength from 0.1- to 5.0N, dried, and kept for 46 days. Regardless of the strength of acid applied, all strips finally contained approximately 3.3 grams of hydrochloric acid per 100 grams of dry leather, and all showed a loss in tensile strength of approximately 25 percent. The volatility of the acid had apparently been responsible for setting up an equilibrium ratio of acid to leather, practically constant for all strips. The ability of the leather to lose hydrochloric acid in this way explains why this acid has not been found responsible for the destructive action so often attributed to sulfuric acid.

When the effect of difference in volatility was eliminated by keeping the leather samples under acid solutions of definite concentrations, hydrochloric acid proved to be more destructive of both kinds of leather than sulfuric acid in solutions of relatively high concentration.

Fig. 460 shows the comparative destructive action of hydrochloric and sulfuric acids on chrome calf leather. This leather was neither colored nor fatliquored

and contained 8.5 grams of chromic oxide per 100 grams of hide substance. Strips of the leather were put into test-tubes, covered with acid solutions of different strengths, corked, and kept in a thermostat at 25° C. Constancy of the concentration of acid in each tube was guaranteed by replacing frequently with fresh solution. The time required for complete disintegration of the leather was recorded. It is noteworthy that the end point in each test was very sharp. The strip would appear intact up to the day of its disintegration, when it would suddenly start to go to pieces and the destruction would be complete within the day.

In solutions 3N or stronger, hydrochloric acid is more active than sulfuric acid, while in weaker solutions the reverse is true. The greater activity of sulfuric acid in the weaker solutions seems to be due to its greater detannizing power. The more powerful destructive action of hydrochloric acid in stronger solutions may be due to the fact that it is a stronger acid than sulfuric, or it may be the result of the specific action of the chloride ion, which the writer has found to be very destructive of protein matter in concentrated solution even at the point of neutrality, while sulfates appear to have a preservative action.

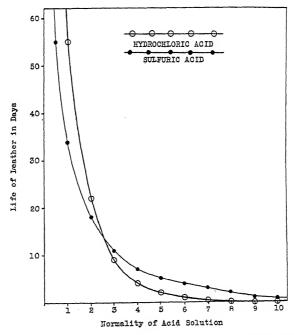


Fig. 460. Time Required for Complete Destruction of Chrome-tanned Calf Leather by Acid Solutions of Different Strengths.

The test-tube experiment was repeated for vegetable-tanned leather, but no destructive action was apparent to the eye with solutions weaker than about 8N. The degree of chrome tannage appeared to have no appreciable effect upon the action of the acid so long as the leather had been sufficiently well tanned to stand the boiling test.

Effect of Relative Humidity

It has been supposed that storing leather containing sulfuric acid in very dry air might accelerate the destructive action of the acid by concentrating it, since the water content of leather decreases with decreasing relative humidity of the atmosphere with which it is in contact. However, Wilson and Kern found that this is not so.

*Following the same technic as that described above, Wilson and Kern treated strips of vegetable-tanned calf leathers with 5 parts of sulfuric acid per 100 parts of dry leather and then aged them in chambers with relative humidities kept constant at 0, 20, 40, 60, 80 and 100 percent, respectively, for 46 days. They then determined the percentage loss in tensile strength at each relative humidity. The results are shown in Table 73.

Table 73. Loss in Tensile Strength of Vegetable-tanned Calf Leathers Containing 5 Parts Sulfuric Acid per 100 Parts Dry Leather after 46 Days' Contact with Atmospheres of Different Relative Humidity.

Relative Humidity (%)	Water in leather (%)	Loss in strength (%)
0	1.25	18.4
20	6.90	33.8
40	9.31	33.5
60	13.28	46.2
80	17.36	51.1
100	30.00	64.1

The increasing destructive action at increasing relative humidities thus appears to be due to the increasing water content of the acid-treated leathers. Lowering the water content of acid-treated leathers actually retards instead of increasing the rate of destruction, contrary to the general supposition.

The mistaken notion as to the expected effect of relative humidity on the destruction of leather by acid may be attributed to confusion between concentration and quantity. The work described above on the action of acids upon chrome- and vegetable-tanned leathers indicates that leather is destroyed only by the free acid and not by the acid which is in chemical combination with the leather. But the leather-acid compound is completely hydrolyzable and will give up all the acid to running water, if sufficient time is allowed. In the experiment under consideration, the ratio of acid to leather was constant for all strips. With increasing water content of any strip the hydrolysis of the leather-acid compound would increase, making the quantity of free acid per gram of leather greater, although the concentration of acid in the water would be less. Apparently, the increase in quantity of free acid is responsible for the accelerated destructive action.

Bowker showed that sole leather tanned with quebracho extract alone does not deteriorate with time unless its content of surfuric acid exceeds 3 percent, but that leather tanned with chestnut-wood extract alone may begin to deteriorate when its content of sulfuric acid exceeds only about 1.5 percent. It is possible that the gallic acid present in chestnut extract produces an effect equal to about 1.5 percent of sulfuric acid and that the effects of the two acids are additive. Oxalic and other non-volatile strong acids are also destructive of leather.

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Glossary of Terms*

Abattoir: A large slaughter house.

Acid dye: A dye whose particles carry a negative electrical charge in water solutions; a dye that will precipitate basic dyes from solution; a dye that will combine directly with chrome-tanned leather without the aid of a mordant.

Acidolene: Trade name for a series of commercial fatliquoring materials.

Acid solution: A solution having a pH value less than 7.0.

Adipose tissue: Fatty tissue.

Air conditioning: Adjusting the temperature and water content of air to serve best

some particular purpose.

Alkaline solution: A solution having a pH value greater than 7.0. Alkanol: Trade name for a series of commercial wetting agents.

Amylase: Enzymes which act upon starches.

Analysis: Separating a material into its component parts, recognizing them and measuring their percentages of the entire material.

Anemometer: A device for measuring the linear velocity of air currents.

Anhydrous: Containing no water; freed from water of crystallization.

Aniline dye: A dye manufactured from coal-tar products.

Aniline leather: Leather finished with transparent finishing materials so that the grain pattern of the leather may be seen.

Anti-blushing agent: A material added to a lacquer to prevent precipitation during the evaporation of the solvents.

Antiseptic: A material that opposes putrefaction or decay by arresting the growth of microörganisms.

Apparent specific gravity of leather: The weight of a given volume of leather divided by the weight of an equal volume of water, making no allowance for voids or air spaces in the volume of leather measured.

Arazym: Trade name for an enzyme preparation for use in unhairing skins.

Areolar tissue: The fibrous and fatty tissues which connect a hide or skin loosely to the underlying parts of the animal body; the flesh.

Areolar-tissue sheath: A tissue thought to enclose hide fibers.

Arkotan: Trade name for a series of commercial syntans.

Ash: The portion of a material remaining after complete burning.

Athlete's foot: A disease of the skin caused by molds.

Atlasol: Trade name for a series of commercial fatliquoring materials.

Autoclave: An apparatus for heating liquids under high steam pressure.

Bacillus (plural: bacilli): A straight-rod bacterium.

Back: A side of sole leather with head and belly removed.

Back boarding: Boarding leather with flesh side in merely to soften it.

Backer: A butcher in a big packing plant who specializes in removing the back, shoulder and base of tail of a hide from the carcass.

Bacterium (plural: bacteria): A microscopic plant consisting of a single cell.

Bark leather: Leather tanned with vegetable-tanning materials.

Bark mill: A machine for grinding raw vegetable-tanning materials for leaching.

Barkometer: An instrument for measuring the weight of a vegetable-tan liquor per unit volume.

Barkometer reading: The same as 1000 subtracted from 1000 times specific gravity. Barretan: Trade name for a series of commercial syntams.

^{*} If a word whose definition is desired is not found in this Glossary, it may be possible to get it by referring first to the Subject Index and then to the page numbers given there.

Basic dye: A dye whose particles carry a positive electrical charge in water solutions; a dye that will precipitate acid dyes from solution; a dye that will combine directly with vegetable-tanned leather without the aid of a mordant.

Basicity: A term used to indicate the available acid in a chromic salt; when pure chromic sulfate is dissolved in water, it produces an acid solution by reacting chemically with the water; more than one-half of the acid thus formed can be neutralized with alkali without causing precipitation of chromium compounds; the percent of total acid producible by the pure chromic salt that has been neutralized is referred to as the percent basicity of the chromic salt.

Basil: An undyed, vegetable-tanned sheepskin.

Basis grades of hides: Standard No. 1 selection of light native cow hides of July, August or September take-off.

Bating: The treatment of unhaired hides and skins with warm solutions of enzymes to remove certain undesirable constituents; formerly, treatment with solutions of fermented hen or pigeon manure.

Baumé hydrometer: An instrument for measuring the weight of a liquid per unit volume.

Beam: A convex wooden slab sloping upward from the floor over which raw stock is placed for trimming, fleshing, unhairing or scudding by hand.

Beamhouse: Department of tannery in which raw stock is washed, soaked, unhaired, bated and prepared for tanning.

Beamster: A worker who scuds the grain of unhaired stock placed over a beam, using a specially designed two-handled knife.

Beaver: An apparatus consisting of two long, heavy planks put together in the form of an inverted V and used in the packing house to scrape the salt off the hair side of hides after curing.

Beeswax: A soft wax obtained from the honeycomb of the common bee and used in making shoe polishes.

Belly: The extreme left or right side of a hide removed by cutting along a line parallel to the backbone line and at such a distance from it as to remove about 23 percent of the total area of the hide for the two bellies; the belly includes the front and hind shank; the line of cutting is determined more accurately for any individual hide by noting the change in feel from the denser structure of the crop to the looser structure of the belly.

Bend: A side of sole leather with head, shoulder and belly removed.

Betanaphthol: A widely used antiseptic and fungicide.

Big-packer hides: Hides flayed and cured in a highly efficient manner by experts in the largest packing plants in the United States.

Binder: A plastic material, like casein, used to hold finely ground pigments together and to cause them to adhere tenaciously to the surface of leather in finishing.

Biobate: Trade name for a series of commercial bating materials.

Bisulfiting: The treatment of hot solutions of vegetable-tanning extracts with sodium bisulfite in order to increase their solubilities.

Bleaching leather: For vegetable-tanned leathers, this usually consists of lightening the color by removing the oxidized tannins and insoluble matter from the outer surfaces with a solution of soda ash. washing and then treating with dilute acid; for chrome-tanned leather, it usually consists of lightening the color by treatment with acid solutions of syntans and sometimes also by precipitating white pigments in the outer surfaces of the leather to give it a white appearance.

Bleeding: Diffusion of uncombined materials from the interior of leather to the outer surfaces where they may contaminate other materials or mar the appearance of the leather.

Blendoyl: Trade name for a commercial mixture of rapeseed and castor oils.

Blood albumin: The dried serum of the blood of cattle used in leather finishes.

Bloom: A deposit of ellagic acid often appearing on the grain surface of leather tanned with chestnut wood or myrobalans extracts.

Blushing: The clouding of the appearance of lacquer finishes caused by precipitation during evaporation of the solvents.

Boarding: Producing a pleasing design on the grain surface of leather and softening it by means of a series of creases produced with the aid of a hand-graining board or by means of a machine designed for the purpose.

Break of leather: The tiny wrinkles formed on the grain surface of leather when it is bent, grain inward; in a fine break there are many fine wrinkles per linear inch; in a coarse break there are fewer wrinkles and they are not so fine.

Brining: Soaking hides, after flaying, in a strong solution of common salt before packing in dry salt, as in the Frigorifico method of curing.

Brisket: The breast of an animal or the portion of the hide over the breast.

Brush coat: The second coat of varnish applied in finishing patent leather.

Brushing: Developing a mild luster on finished surfaces of leather by the action of a rotary brush; freeing the surfaces of leather from fine fibrous dust after buffing by drawing it between a pair of long rotary brushes.

Buck leather: Cowhide upper leather with grain surface buffed and dusted with talcum or finely ground mineral pigments.

Buffering agent: A substance added to a solution to prevent wide changes in pH value during a chemical reaction.

Buffing: The operation of producing a fine nap on the grain surface of leather by means of Carborundum paper or on the flesh side of small skins by the action of an emery wheel; a very thin grain split of leather from cattle hides or skins, used in bookbinding.

Building a hide pack: The systematic salting, folding and piling of hides after flaying to form the pack in which they are allowed to cure for a month or longer.

Bull hide: A hide from an uncastrated male of the ox kind, usually ranging in weight from 75 to more than 100 lbs. in the green, salted state. It is characterized by very thick and rough head, neck and shoulders.

Butcher cuts: Damage to hides and skins caused by improper or unskilled flaying, usually in the form of cuts and furrows on the flesh side.

Butt-branded hides: Hides branded on the butt area back of the break in the flank. Cabretta: The skin of a hybrid cross between a sheep and a goat; a straight-haired sheepskin.

Calgon: Trade name of sodium metaphosphate of high molecular weight used in tanning, water conditioning and in the prevention of discoloration by iron on vegetable-tanned leathers.

Calorie: The quantity of heat required to raise the temperature of one gram of water by 1° C.

Candelilla wax: A hard wax occurring as an excretion on desert plants along the United States-Mexican border and sometimes used as a substitute for carnauba wax.

Carding: Combing and brushing the wool of fur skins.

Carnauba wax: An exudation from the leaves of the carnauba palm, Copernica cerifera, which grows in Brazil; Brazil wax; a hard wax widely used in leather finishes.

Carpincho: Skin of a South American water rodent often classed as a pigskin. Casein: A protein substance obtained from milk and widely used as a plastic in leather finishes.

Centigrade, degrees (°C.): A temperature scale on which the freezing point of water is recorded as zero and the boiling point as 100. To convert degrees Centigrade to degrees Fahrenheit, multiply by 1.8 and add 32.

Chamoising: Tanning skins by means of cod-liver oil.

Chamois leather: Leather produced from pickled sheepskin fleshers by tanning with cod-liver oil.

Cheeking: Reducing the thickness of the heads of unhaired skins by splitting.

Chestnut blight: A fungous disease of the American chestnut tree of the southeastern states that is threatening its extinction.

Chlorine: A greenish yellow, poisonous gas with suffocating odor, used as a disinfectant; usually sold as a liquid under pressure in metal cylinders.

Chrome liquor: A solution of basic chromic salt used in chrome tanning; usually made by treating a strong solution of sodium dichromate with a reducing agent, such as sulfur dioxide or a mixture of glucose and sulfuric acid.

Chrome retanning: Tanning raw stock first with chrome liquor, washing and then retanning with vegetable-tanning materials.

Chrome tanning: The conversion of raw hide into leather by treatment with water solutions of complex salts of chromium.

Chromic oxide: A green, water-insoluble oxide of chromium. Because of the complex and variable nature of the chromium compounds present in leather and liquors, it is customary to measure their amounts in terms of the amount of chromic oxide they would produce if converted into chromic oxide.

Chromite: An ore consisting of 68 percent chromic oxide and 32 percent iron oxide, from which sodium dichromate is prepared.

City-butcher hides: Hides from animals not slaughtered, flayed and cured in packing houses, but in city abattoirs or by city butchers.

Clearer-out: A butcher in a big packing plant who specializes in the removal of the hide from the fore legs and under the sides of the neck.

Coccus (plural: cocci): A spherical bacterium.

Cockle: A warty growth in sheepskins.

Collagen: The protein material of the hide fibers.

Collatone: Trade name for a powerful disinfectant and fungicide.

Colloidal clay: A clay used in the ceramic industry so finely divided that it remains in suspension when mixed with water; used in fatliquoring some upper leathers to produce fullness and mellowness, in making white leathers and in the oil-wheeling of sole leather.

Colophony: Common rosin.

Colorado steer hide: A steer hide branded on side or butt; not necessarily from Colorado.

Color index: A large book describing practically all aniline dyes manufactured and assigning to each a color-index number by which it can be identified and its sources determined; published by the Society of Dyers and Colourists, Bradford, England.

Combined tannin in leather: Tannin that has combined so vigorously with the hide protein that it cannot readily be removed by washing.

Combined water-soluble matter in leather: Material present in a state of loose chemical combination with the leather than can be removed from the finely ground leather only by prolonged washing.

Contract unit for hides: A certificated lot of 40,000 lbs. (plus or minus 5 percent) of hides of one grade.

Copperas: Light green crystals of the sulfate of ferrous iron.

Cordovan leather: Leather made from the butt or shell of a horsehide.

Corium: The derma or true skin; the part of the thickness of a hide or skin which excludes the epidermis, hair and flesh; the part that is converted into leather.

Corrected grain: The grain surface of leather snuffed so lightly as not to destroy the grain pattern.

Correct pattern: The contour of a hide flayed so as to permit the tanner to produce the maximum amount of good leather from it; a standard pattern adopted by packers and tanners.

Country hides: Hides of animals not slaughtered, flayed and cured in packing houses, but by farmers and country butchers.

Crocking: The rubbing off of coloring or finishing materials from leather onto other materials.

Crop: A side of sole leather with belly removed.

Cropping: Cutting the bellies from sole-leather hides and sides after tanning in the layer vats.

Crusting: The storage of dry leather for conditioning or aging, during which time it takes up water from the air until it reaches equilibrium with the relative

humidity of the air; some of its constituents become more uniformly distributed throughout the thickness of the leather, and greater fixation of the tanning materials may occur.

Crusty break: A break of leather in which the wrinkles are coarse, sharp and generally displeasing to the eye; finish break.

Curing: Saturating raw hides and skins with common salt to retard bacterial action and putrefaction.

Currying: Incorporating oils and greases into leather and otherwise preparing it for service.

Cutch extract: A water-soluble tanning substance obtained by extracting the bark of several varieties of mangrove tree.

Cuticle: The epidermis.

Dark-field illumination: A special technic developed in microscopic work to make the object appear brilliantly illuminated on a black background.

Daub coat: The first coat of varnish applied in the finishing of patent leather.

Deacons: Very small calfskins.

Degreasing: Removing the greases from; in the case of pickled sheepskins by drumming the stock with kerosene, water and salt; in the case of leather by extracting the dry leather with naphtha.

Degree of tannage: The number of lbs. of tannin combined with 100 lbs. of hide protein.

Derma: The corium or true skin.

Developed dyes: Dyes whose colors are developed after applying to the leather, by treatment with sodium nitrite; used on suède leathers to prevent crocking.

Dewclaw: An undeveloped toe in cattle.

Dewlap: The hanging skin under the throat of cattle, where the butcher first inserts his knife in the slaughter.

Diethylene glycol: Organic solvent used as a plasticizer in leather finishes.

Dimensional changes in leather: The increase or decrease in thickness and area of leather with increasing or decreasing relative humidity of the atmosphere.

Dimethylamine: A commercial sharpening agent for lime liquors.

Diplococci: Pairs of spherical bacteria.

Direct dye: A dye that will combine directly with chrome-tanned leather without the aid of a mordant.

Directional ventilating power: A ventilating power of leather that is greater for passing water from the flesh side to the grain side than from the grain side to the flesh side.

Disinfectant: An agent added to a material to destroy the microörganisms it contains or to free it from other infection.

Dowicide: Trade name for a series of commercial fungicides.

Drawn flanks: Flanks of skins and leather that have shrunk and show furrowed lines on the grain surface over the underlying blood vessels.

Drenching: A method of deliming and acidifying unhaired skins by immersion in a water infusion of fermenting bran.

Drum: A revolving cylindrical container for hides and skins, usually equipped inside with pegs for lifting the stock, used for such operations as washing, tanning, dyeing, fatliquoring and stuffing.

Drumming: Tumbling hides and skins or leather in a revolving drum.

Dry dip: A strong solution of vegetable-tanning extracts in which dry sole leather for finders' bends is dipped, preparatory to the second bleaching and second oil-wheeling, to increase the firmness and solidity of the finished leather and to add weight.

Drying tunnel: A tunnel in which damp leather is placed for drying in a current of air, often with temperature and relative humidity controlled.

Dry loft: A space in a tannery where dried leather is kept for crusting or stored awaiting selection for subsequent treatment.

Dry milling: Tumbling pressed leather in a revolving drum to open it up and remove the creases.

Dubbin: A mixture of cod oil and tallow.

Duponol: Trade name for a series of commercial wetting agents; used in degreasing sheepskins, tanning, dyeing and finishing.

Dusting: Spreading ground raw vegetable-tanning materials over and between hides entering the layer vats to add to the tannin strength of the liquors; a common method before the days of concentrated tanning extracts.

Dye indicator: A solution of dye whose color changes over a definite range of pH value; used in the colorimetric measurement of pH value.

Egg albumin: The dried whites of hens' eggs used in leather finishes.

Egg yolk: Deshelled whole eggs treated with 20 percent by weight of common salt as a preservative; salt-free egg yolk is treated with no common salt but with small percentages of sodium bifluoride or other powerful preservative; used in fatliquoring colored, chrome-tanned light leathers.

Elastin: The yellow connective tissues of the skin which furnish structural support for the blood vessels and thermostat mechanism.

Elk leather: A name applied to chrome-retanned cowhide shoe-upper leather treated with greases to make it soft and water-repellant.

Embossing: Producing patterns in relief on the grain surface of leather by means of embossing plates applied in a press under great pressure.

Emullo: Trade name for a series of commercial lacquer emulsions in water.

Emulsion: Microscopic droplets of one liquid distributed throughout another liquid in which it is insoluble, as the globules of butter fat in the water of milk.

Enamelled leather: Patent leather.

Enzymes: Substances secreted by living cells which bring about hydrolysis of other substances in amounts vastly greater than the amounts of enzymes required.

Epidermis: The cuticle or outer layer of epithelial tissue that covers the derma and is removed during unhairing.

Epithelial tissue: The cellular tissue that covers all free surfaces within and without the animal body.

Equilibrium: A state of balance in chemical reactions after attainment of which there is no further change with time.

Erector-pili muscle: One of the tiny muscles of the skin that cause goose pimples to form, the hair to stand on end, and oil to flow from the sebaceous glands to the skin surface; a muscle active in the thermostat mechanism of the skin.

Ethanol: Pure grain alcohol.

Etonal: Trade name for a series of commercial finishing materials.

Ex-light steer hide: One weighing from 30 to 48 lbs. in the green, salted state.

Extracting: Drumming wrung sole leather from the layer vats with a concentrated vegetable-tanning extract to incorporate into it as much vegetable-tanning material as it will hold.

Fahrenheit, degrees (° F.): A temperature scale on which the freezing point of water is recorded as 32 and the boiling point as 212. To convert degrees Fahrenheit to degrees Centigrade, subtract 32, and divide the difference by 1.8.

Falling: Decreasing plumpness of a hide or skin, in which it tends to become increasingly soft and flaccid.

Fatliquoring: Applying oils to leather in the form of dilute oil-in-water emulsions. Fell: A hide or skin.

Fellbeater: A butcher in a big packing plant who specializes in the removal of the hide from a carcass over the areas where it adheres tightly at the front of the round and flank.

Fellcutter: A butcher in a big packing plant who specializes in the removal of the hide from a carcass over the areas from the tail to the hind legs.

Fellmonger: A dealer in hides and skins.

Fermentation: Chemical changes in organic matter brought about by microörganisms. Fiber sarcolemma: A tissue supposed to enclose hide fibers.

Fibril: A filament of protein, many of which constitute a hide fiber.

Fibroblasts: The white corpuscles of the blood that spin the filaments of protein called fibrils and that are responsible for the growth of hide fibers by repeated additions of fibrils.

Fibroid tumor: An abnormal growth of collagen fibers due to the excessive activity of the fibroblasts.

Finders' leather: Very heavy, firm and dense vegetable-tanned sole leather, used by cobblers.

Finish break: A crusty break of leather attributable to improper finishing.

Finishing: Treating leather so as to make it more pleasing to the eye and more serviceable in use; applying a plastic coating to the grain surface of leather to give it a finished appearance.

Firmness of leather: The force required to bend a standard strip of heavy leather through an arc of given radius of curvature; that is, so that the grain surface forms an arc of that of a circle of given radius.

Fixation value: The relative speed or vigor of combination of different vegetable tannins with hide substance as measured by the relative amounts which combine under a standard set of conditions; avidity of combination.

Fixed tannin: Same as combined tannin.

Flaccid: Flabby: lacking firmness as in a bated hide or skin.

Flagella: Thin thread-like processes which serve to propel bacteria with a corkscrew motion.

Flanks: The portion of a hide or skin corresponding to the definition for bellies.

Flaxseed mucilage: The mucilage extracted from ripe flaxseed with hot water and used as a plasticizer in leather finishes.

Flaying: The removal of the hide or skin from an animal carcass.

Flesh: The side of a hide or skin opposite the hair or grain side; the areolar tissues on the flesh side.

Flesher: Sheepskin after removal of grain layer or skiver.

Fleshing: The operation of removing the areolar tissues from the flesh side of hides and skins.

Flint hides: Hides dried without curing.

Floorsman: A butcher in a big packing plant who specializes in the removal of the hide from a carcass over the bellies.

Fluorex: Trade name for a mixture of sodium bifluoride and sodium silicofluoride used to disinfect hides and skins from restricted countries.

Flywing grain: A very thin grain split from a sheepskin.

Follicle: The pocket or indentation of the skin surface in which the hair grows.

Follicular mange: A parasitic skin disease of animals caused by a mite which lives in the hair follicles and below the skin surface.

Formalin: A 40 percent solution of formaldehyde; a tanning agent; often used as a hardening agent for casein in leather finishes.

Free water-soluble matter in leather: Soluble matter that can be removed from finely ground leather with very little washing.

French chalk: talc; finely powdered magnesium silicate.

Frigorifico hides: Hides from South America corresponding to big-packer hides in the United States.

Frized leather: Very soft glove leather made from skins limed for a month or longer during which time the entire supporting structure of elastin in the grain layer is destroyed.

Fulling stocks: Kickers; a machine used in chamoising for mixing cod-liver oil intimately with the pickled fleshers.

Function: In mathematics, one quantity is a function of another when for each value of the latter there corresponds a definite value of the former.

Fungi: Microscopic vegetable plants which include the yeasts; molds and mildews.

Fungicide: A destroyer or killer of molds.

Fungizyme: Trade name for a series of commercial bating materials containing fungous enzymes.

Fungous enzymes: Enzymes secreted by molds.

Fustic: A yellow natural dye extracted from the yellow Brazil wood of the species *Morus tinctoria*.

Futures contract: A standard contract used in the sale of hides for future delivery through Commodity Exchange, Inc.

Gain of leather: Same as yield of leather.

Gardinol: Trade name for a series of commercial wetting agents; used in the fatliquoring of white leathers.

Gelatin: A dried protein jelly obtained by treating calfskin with boiling water.

Glass electrode: A complex electrical equipment by means of which pH values of solutions are measured simply and accurately.

Glassy layer: The dense fibrous structure found in the butts or shells of horse hides. Glauber's salt: Sodium sulfate containing water of crystallization; a salt used in some tannery operations; anhydrous Glauber's salt is a much more concentrated form with water of crystallization removed.

Glazing: Producing a glassy surface on finished leather by the frictional action of a non-rotating solid glass cylinder drawn across the grain surface under high pressure.

Glazing jack: A machine for glazing leather.

Glue stock: Waste trimmings of raw hides sold for manufacture into glue.

Glyco Neats: Trade name for certain commercial neatsfoot-oil mixtures used in fatliquoring.

Goldbeater's skin: The membrane of the blind gut of the ox between the large and small intestine.

Gold leather: Leather with grain surface covered with pure gold leaf.

Goulac: Trade name for a by-product of the paper industry used as a filling material for vegetable-tanned sole leather.

Graining: Boarding.

Grain layer: The layer of the derma of hides, skins and leather that includes the hair follicles; the thermostat layer.

Grain pattern: The design on the outer surface of leather produced by the arrangement of hair follicles and pores, characteristic of the kind and age of animal.

Grainy leather: Leather showing marbled grain.

Grassers: Rough-necked calfskins from underfed animals.

Grubby hides: Hides damaged by grubs of the warble fly, which lays its eggs on the animals hairs, from which they enter the hide and mature, leaving unsightly holes, scars and other damage; pepper boxes.

Hair slips: Hides and skins that have suffered sufficient putrefaction to loosen the hair.

Handler vat: A vat containing vegetable-tan liquor into which vegetable-tanned skins are thrown for further tanning after coming from the stick vats and removal from the sticks.

Head: The portion of a hide or skin from the head of the animal.

Header: A butcher in a big packing plant who specializes in the removal of the hide only from the head and face of the carcass.

Head splitting: same as cheeking.

Head vat: The tanning vat in a series that contains the strongest tan liquor; usually the vat from which the stock is taken from a series after vegetable tanning.

Heavy hide: A steer hide weighing more than 58 lbs. or a cow hide weighing more than 53 lbs. in the green, salted state.

Hedging: Making a bet to offset a bet already made; selling hides for future delivery to offset a possible drop in market value of an inventory of hides and leather.

Heifer: A young cow.

Hematine: An oxidized natural dye obtained from logwood.

Hide: The outer covering of a large animal; among cattle hides, one weighing more than 30 lbs. in the green, salted state.

Hide dropper: A butcher in a big packing plant who specializes in the removal of the hide from the carcass only from the neck and shoulders.

Hide spreader: A workman who assists in the building of a hide pack in the curing of hides in a big packing plant.

Hind-legger: A butcher in a big packing plant who specializes in the removal of the hide only from the hind legs of the carcass.

Horse: A portable wooden vehicle on which leather and skins are piled for draining or for transportation from one department to another.

Horsing: Piling leather or skins on a wooden horse.

Hot-air stuffing mill: A drum equipped with a system for heating its contents to any desired temperature; used in stuffing leather with molten greases.

Hyaline layer: A tissue assumed to be present between the epidermis of a hide and the surface of the grain layer.

Hydraphtal: Trade name for a commercial material used in degreasing to assist in the penetration of the degreasing solvents into the skins.

Hydrolysis: Chemical decomposition in which water is involved in the chemical reaction.

Hygrometer: A device for measuring the relative humidity of air.

Hypernic: A red natural dye extracted from the red Brazil wood of several species of Caesalpinia.

Hypo: Sodium thiosulfate; used in the second bath of the two-bath chrome-tanning process to reduce the sodium dichromate to the condition of a chrome-tanning agent; used as a neutralizing agent for acids; it is characterized by the production of finely divided sulfur when used for these purposes.

Inconel: Trade names for a non-corrosive alloy of nickel and chromium used for making drums and vats where a high resistance to corrosion is important.

India tannage: A vegetable tannage peculiar to India and often used on stock to be exported from India.

Infection: The invasion of a tissue or other material by bacteria or other harmful microörganisms.

Ion: An electrically charged atom or group of atoms.

Irish moss: The mucilage extracted from a seaweed found along the coasts of Ireland and New England and used as a plasticizer in leather finishes.

Iron (as a measure of thickness): $\frac{1}{48}$ inch.

Ironing: Smoothing the grain surface of finished leather and adding a pleasing appearance by means of a hot iron.

Isinglass: A pure gelatin obtained from the swimming bladders of various fish.

Japanned leather: Patent leather.

Japan wax: A soft wax obtained from the berries of several varieties of plants found in Japan and used in shoe polishes.

Keratin: The protein material of the hair and epidermis.

Keratose: A degradation product of keratin.

Kickers: same as fulling stocks.

Killing: Treating wool with soda-ash solution or other material to prepare it for dyeing.

Kip: The outer covering of an animal intermediate in size between a skin and a hide; among cattle hides, one weighing between 15 lbs. and 25 lbs. in the green, salted state.

Kiss spot: A light spot on vegetable-tanned leather caused by contact with another hide, preventing free access of the tan liquor to it.

Knee staker: A metal blade set in a wooden support over which small skins are worked, using the hands and the knee, for staking them.

Knocker: The butcher who stuns the animal by a crushing blow on the head before the slaughter.

Koreon: Trade name for a series of commercial one-bath chrome-tanning materials. Kosher hide: Hide of an animal killed according to the Rabbinical law, the cutting of the throat interfering with the production of a hide of standard pattern: a cut-throat.

Lacquer: A nitrocellulose finishing material for leather.

LacTan-X: Trade name for a commercial vegetable-tanning material made by fermenting sulfite liquors from paper mills with bacterial cultures to produce lactic and acetic acids.

Latent heat of vaporization: The number of calories of heat required to change one gram of a liquid to vapor without changing its temperature.

Layaways: The layer vats used in tanning sole leather.

Layer vat: A vat of relatively strong vegetable-tan liquor into which sole-leather hides are thrown after preliminary tanning in rocker vats.

Laying-away: Storing hides in layer vats for a long time to insure completeness of the tannage; where only weak liquors are available, the hides are dusted with ground raw vegetable-tanning materials to provide a sufficient amount of tannin.

Laying-bye: Covering a hide pack with salt in curing and letting it stand so that the strong brine formed will seep through the entire pack.

Leach-casting machine: A mechanical device set in leaching vat to facilitate removal of the ground vegetable-tanning material after extraction of its tannin by hot water.

Leach house: The department of a tannery where raw vegetable-tanning materials are extracted with hot water and where vegetable-tanning extracts are dissolved in water to make strong stock liquors for the tan yards.

Leaching: Extracting the tannin from ground raw vegetable-tanning materials by means of hot water.

Leather: Animal hide or skin so treated chemically as to make it permanently more resistant to decomposition, particularly when wet, and to make it serviceable.

Leather gauge: An instrument for measuring the thickness of leather in ounces or millimeters.

Leatherlubric: Trade name for certain commercial sulfonated-oil compounds used in fatliquoring.

Lecithin: A phosphorus-containing fatty substance found in egg yolk, soybeans and other materials and found to be useful in fatliquoring leather.

Legger: A butcher in a big packing plant who specializes in skinning the legs of the carcass and removing the shin bones with hoofs attached.

Leukanol: Trade name for a series of commercial syntans; the first syntan to be produced commercially in the United States.

Licensed warehouse: A warehouse licensed for the storage of hides upon recommendation of the Committee on Grading and Warehousing and with the approval of the Board Hide Trade Group of Commodity Exchange, Inc.

Light hide: A steer hide weighing from 48 to 58 lbs. or a cow hide weighing from 30 to 53 lbs. in the green, salted state.

Lime-fleshing: Fleshing hides and skins after the liming operation.

Lime liquor: A saturated limewater containing lime greatly in excess of saturation and used for loosening the hair of hides and skins.

Lime slaking: The appropriate treatment of caustic lime or calcium oxide with water to produce slaked lime or calcium hydroxide for use in liming.

Lipase: Enzymes which act upon fatty materials.

Logwood: A natural dye extracted from campeachy wood (Hematoxylon campechianum).

Lustrone colors: Trade name for certain commercial nitrocellulose finishes colored with dyes.

Macroscopic: Large enough to be seen without the aid of a microscope.

Magnification: The number of times one dimension is increased of the image enlarged by means of the microscope; usually expressed as diameters.

Malpighian layer: Layer of epithelial cells in the epidermis next to the grain surface of the derma.

Mange: A parasitic skin disease of animals.

Manufacturers' leather: Vegetable-tanned sole leather sold to shoe manufacturers that is not quite so heavy, firm and dense as the finders' leather sold to cobblers.

Marbled grain: A mosaic pattern of indentations sometimes occurring on the grain surface of leather corresponding to the pattern of the network of tiny underlying blood vessels; a rough appearance of the grain surface displeasing to the eye; wild grain; graininess.

Matadero hides: South American hides corresponding in quality to country hides in the United States.

Matrix: A mold built on the bed of an embossing press to sharpen the design of the pattern produced on leather by the embossing plate.

Maxwhite: Titanium dioxide ground in casein solution, sulfonated castor oil and paraffin oil for use in the fatliquoring and finishing of white leathers.

Merpol: Trade name for a series of commercial wetting agents.

Mertanol: Trade name for a series of commercial syntans.

Methanol: Pure wood alcohol.

Micron: A measure of length equal to 0.001 millimeter, or 0.0000394 inch.

Microörganism: A tiny living cell or form of life that is too small to be seen by the unaided eye, but can usually be seen when highly magnified by means of a microscope.

Microscope: An optical instrument consisting of series of lenses and an illuminating system for magnifying minute structures for visual inspection or for photographic records.

Microscopic: Too small to be seen clearly without the aid of a microscope.

Mineral oil: Colorless, non-volatile oil obtained from petroleum: paraffin oil.

Moellon degras: A valuable emulsifying agent and fatliquoring material obtained as by-product from the cod-liver oil used in chamoising sheepskins.

Mold: Multicellular microscopic vegetable plants which form cobweb-like masses of branching threads from the surface of which tiny fertile threads project into the air bearing the part of the plant from which the spores develop, which may be of brilliant colors, black or white, according to kind of mold.

Montan wax: A hard wax obtained from the lignites or brown coal of Saxony and Thuringia and sometimes used as a substitute for carnauba wax.

Mordant: A material that will combine chemically with leather and then combine with a dye to bring about a combination of the dye with leather.

Morocco leather: Fancy vegetable-tanned goatskin leather with a distinctive natural grain pattern.

Muriatic acid: Hydrochloric acid.

Naphthalene: A tar camphor often spread among dried goatskins to lessen the danger of attacks by insects during shipment and storage.

Native hide: A hide that has not been branded.

Natural dye: A dye obtained by the extraction of wood or other colored form of vegetable material.

Neomerpin: Trade name for a series of commercial wetting agents.

Neutralizing agent: A substance added to an acid or alkaline solution to bring its pH value nearer to 7.0.

Neutral solution: A solution having a pH value of approximately 7.0.

Neutrigan: Trade name for a commercial neutralizing agent for chrome-tanned leather with special properties.

Nontannin: The portion of the water-soluble matter in a vegetable-tanning material other than tannin that is non-volatile.

Nopco: Trade name for a series of commercial oil products used in fatliquoring and treating leathers.

Nopcowite: Trade name for a commercial fatliquor for white leathers. Nutricod: Trade name for a commercial blend of cod and mineral oil.

Offal: Parts of hides and skins rejected for making standard grades of leather; refers sometimes also to heads, shoulders and bellies of heavy leathers to differentiate them from the more valuable bends.

Oiling off: Coating the grain surface of wet leather with oil before drying.

Oil of eucalyptus: An antiseptic used in leather finishes.

Oil of mirbane: An antiseptic used in leather finishes.

Oil of sassafras: An antiseptic used in leather finishes.

Oil of thyme: An antiseptic used in leather finishes.

Oil-wheeling: Drumming sole leather after extracting, tempering, bleaching and wringing with various materials to increase the yield of leather and improve its properties.

One-bath process: A process in which raw stock is tanned directly with chrome liquor. Oropon: Trade name for a series of commercial bating materials; the original enzyme bate used to replace the obnoxious dungs.

Orthochrom: Trade name for certain commercial finishing materials containing colored pigments in nitrocellulose lacquers.

Orthoclear: Trade name for certain lacquer finishing materials without colored pigments.

Osage orange: A natural dye and tanning material extracted from the wood of the osage orange tree (Maclura pomifera).

Ounce (as a measure of thickness): 🕏 inch; originally it meant the thickness of 1 square foot of leather that weighed 1 ounce avoirdupois.

Overflow liquor: The vegetable-tan liquor that flows out of a system of connected vats when one of the vats is strengthened by the addition of stock liquor.

Overflow vat: A vat used to receive and store overflow liquor from a series of tanning vats.

Overshot buffer: A machine equipped with an emery wheel for buffing the flesh side of damp, small skins, as in the making of suède leather.

Overweight kip: A cattle hide weighing from 25 to 30 lbs. in the green, salted state. Ox: A name used to designate domestic cattle.

Ox blood: The whole blood of cattle used in leather finishes.

Oxidizing agent: A material that changes the chemical composition of another material by adding oxygen to it.

Pacific Coast hide: Hide of an animal slaughtered, flayed and cured in one of the recognized packing plants on the Pacific Coast.

Packer hide: Hide of an animal slaughtered, flayed and cured in a recognized packing plant.

Paispearl: Trade name for certain commercial pearl essences obtained from fish scales and used to finish leather with a pearly appearance.

Pancreatin: Enzymes obtained from the pancreas of an animal; trypsin.

Pancreol: Trade name for a series of commercial bating materials.

Paranitrophenol: A disinfectant and fungicide.

Pasting: The pasting of damp leather to a smooth plate for drying it in a smooth and stretched-out condition.

Patent leather: Leather finished with several coats of linseed-oil varnish; sometimes also given a top coat of lacquer; japanned leather; enameled leather.

Pattern of a hide: Contour of a hide when laid out flat.

Peccary: Skin of the wild boar found in tropical America; South American pigskin.

Penetration: The diffusion of a material into the thickness of a hide or piece of leather.

Pepper box: The pattern produced on the grain surface of leather from grubby hides by the grub holes, which often resemble buckshot marks.

Phosphorated oils: Oils treated with phosphorous pentoxide to endow them with special characteristics.

Photomicrograph: Photograph taken through a microscope of a microscopic object so highly magnified that it can be seen in detail with the unaided eye.

pH value: A measure of the vigor of the acid or alkaline reaction of a solution, where 7.0 represents a neutral solution; values decreasing from 7.0 represent solutions of increasing acidity and values increasing from 7.0 represent solutions of increasing alkalinity.

Pickling: Saturating unhaired hides and skins with a solution usually of sulfuric acid and common salt to preserve them or to prepare them for tanning, although other acid and salt combinations are sometimes used.

Pigment: A finely ground, opaque, colored material insoluble in water often added to leather finishes to provide color and to hide defects in the grain surface of the leather.

Pigment leather: Leather finished with finishing materials containing opaque pigments which hide the grain pattern and any defects it may have.

Pigskin strips: Rectangular pieces of pigskin from over the lard areas of the animal sold to the tanners by the packers; the rest of the skin is usually left on the meat.

Pile-up: The volume of leather per unit weight; the number of square feet of leather 8 irons thick per 100 lbs. of leather of 12% moisture; 115.5 divided by the apparent specific gravity of the leather of 12% water content.

Pipey leather: Leather whose grain surface forms coarse, sharp and loose wrinkles, displeasing to the eye, when it is bent grain inward.

Plastic: Capable of being molded, soft and pliable; a material that can be shaped when soft and hardened afterward.

Plasticizer: A material that is added to another to keep it soft and pliable.

Plating: Producing a smooth grain surface on leather by pressing it on a bed with a smooth, heated metal plate under very high pressure.

Poor pattern: Outline or contour of a hide not conforming to the standard or correct pattern adopted by packers and tanners.

Porosity: The ability of a leather to pass air from an atmosphere of higher to one of lower pressure.

Post-mortem changes: Chemical and structural changes that naturally occur in a hide between the time of slaughter and that of the curing or other preservative operation.

Pressing: Removing the bulk of water from wet leather by means of a hydraulic press.

Press-over system: A system of pump logs so arranged in a series of connected tanning vats that the addition of stock liquor to the head vat in the series causes an equal volume of liquor to flow from one vat to another so that an equal volume of weak liquor overflows from the tail vat.

Primal: Trade name for a series of commercial finishing materials containing synthetic resins.

Pritch pole: A pole used to hold the carcass of an animal upright during the flaying operation.

Properties: The characteristics of a substance.

Proteases: Enzymes which act upon proteins.

Puering: Now included under the term bating; formerly the treatment of unhaired skins with solutions of fermented dog dung to remove certain undesirable constituents and to prepare the skins for tanning.

Puer shop: Bating department of the beamhouse.

Pulling a hide pack: This is just the reverse of building a hide pack and involves taking the pack apart and bundling the hides for shipment.

Pump log: A heavy wooden conduit used for transferring vegetable-tan liquors from one vat to another.

Purity: The parts of tannin per 100 parts of water-soluble solid matter in a mixture containing vegetable-tanning materials.

Putting out: Same as setting out.

Pyroxylin: Nitrocellulose.

Quercitron: A natural dye extracted from the ground inner bark of the Baltimore oak (Quercus tinctoria, nigra).

- Quinone: An organic solid of irritating properties, slightly soluble in water, capable of combining with hide substance to produce a leather resistant to the action of boiling water.
- Randall & Stickney gauge: Trade name for a precision gauge for measuring the thickness of leather accurately to 0.001 inch.
- Rayox: Trade name for a series of commercial titanium dioxide white pigments.

 Reducing agent: A material that changes the chemical composition of another material by taking oxygen from it.
- Relative humidity: The number of parts of water in the air per 100 parts of water in the same volume of saturated air at the same temperature.
- Relative-humidity tables: Tables from which the relative humidity of air can be found by noting the value given at the intersection of two columns of figures, one headed by the wet-bulb temperature of the air and the other by its drybulb temperature.
- Residue: The material left after the complete evaporation of water or other solvent from a solution.
- Resilience of leather: The percentage rebound of a standard plunger dropped onto the leather surface under standard conditions.
- Resistance of leather to acid: The maximum percentage of acid that the leather may contain without deteriorating with time.
- Resistance to grain cracking: The extent to which leather may be stretched or bent without causing the grain surface to crack.
- Restricted countries: Countries from which imports of hides and skins are permitted only under the sanitary regulations of the Bureau of Animal Industry.
- Reticular layer: The fibrous portion of a hide or skin between the grain layer and the flesh.
- Reticulin: Tiny fibrils that appear to bind collagen fibrils together in a fiber.
- Rocker vat: A vat for the preliminary vegetable tanning of sole leather in which the frame for holding the leather is equipped with a rocking device to prevent the hides from touching one another during tannage, thus preventing kiss spots.
- Rolling: Subjecting the grain surface of leather to the action of a metal roller under pressure to smooth it, compress it and generally improve its appearance.
- Rolling jack: A machine for rolling leather under pressure.
- Rosin: A sticky light-yellow to red-brown material obtained by distilling off the more volatile turpentine from crude turpentine; abietic acid; used to produce waterproofness and tackiness in leather, as in golf-grip leather.
- Rubber latex: A juice secreted by the rubber tree to aid in healing damage to the tree; an emulsion of rubber in water; used as a binder in leather pigment finishes.
- Rumper: A butcher in a big packing plant who specializes in cutting the hide away from the base of the tail and rump of the carcass.
- Run pelts: Sheepskins dewooled by sweating whose grain surfaces have been pitted or liquefied in spots by worm-like organisms.
- Russia calf: Vegetable-tanned calf leather scented with birch oil; originally calfskins tanned in Russia with birch-bark extract.
- Saladero hides: South American hides corresponding in quality to small-packer hides in the United States.
- Salometer: An instrument for measuring the weight of a salt solution per unit volume and thus giving a measure of its salt content; used in strengthening pickle liquors with salt.
- Salt stains: Discolorations on the grain surface of hides and skins caused by improper or delayed curing.
- Salt thrower: A workman in a big packing plant who specializes in spreading rock salt over the hides during the building of a hide pack for curing.
- Sam, sammie, sammy: To condition leather with water to bring about a uniform distribution of water in the leather of about 30 to 40 percent by weight; to dampen leather in sawdust; to case leather.

Santobrite: Trade name for a commercial fungicide.

Saturated air: Air containing the maximum amount of water that it can dissolve at any given temperature.

Scabies: A contagious skin disease caused by a parasitic mite.

Scored hides: Hides damaged during flaying by cuts that do not completely penetrate them.

Scotch grain: A pebbled pattern given to the grain surface of leather by embossing. Scud: Remnants of epithelial tissues, hair pigment, etc., left in the grain layer of hides and skins after unhairing.

Scudding: Removing the scud from unhaired hides and skins by the scraping action of a knife or blades by hand or by machine.

Sebaceous glands: The oil-producing glands of the skin located in the grain layer.

Sebum: The fatty materials of the sebaceous glands of the skin.

Selection factors: Condition of hides as to soundness, good cure, pattern, and freedom from defects, etc., as relates to stock bought or sold on futures contracts. (See By-laws of Commodity Exchange, Inc., in Chapter 6.).

Setting out: A method for removing the bulk of water from wet leather while smoothing it by hand or by machine preparatory to drying it.

Shagreen: Epidermis of shark skin.

Shank: The part of a hide or skin from a leg of the animal.

Sharpening agent: A material added to a lime liquor to accelerate the loosening of the hair or hides and skins immersed in it.

Shaved weight: The weight of a pack of leather taken after shaving or when its water content is about 50 percent.

Shaving machine: A machine for reducing the thickness of leather or smoothing the flesh side by the cutting acton of sharp blades set spirally in a revolving cylinder.

Shearling: Sheepskin or lambskin tanned with the wool on for garments or slippers. Shell: The butt of a horsehide containing the dense mass of fibers known as the glassy layer, which gives cordovan leather its characteristic properties.

Shellac: A thick excrescence found on the small twigs of several species of East Indian trees, resulting from the bite or sting of the insect Coccus lacca; widely used in leather finishes to produce luster.

Shirlan: Trade name for a commercial odorless fungicide.

Shoulder: The portion of a hide in front of a line drawn perpendicular to the backbone line just back of the fore legs, but not including the fore shanks; when the head is removed, it is known as a headless shoulder.

Shrink temperature: The temperature of water at which a strip of leather placed in it begins to shrink, which is different for each kind and degree of tannage.

Side: One-half of a hide or skin cut in two along the line of the backbone.

Sig water: An alkaline solution of soda ash, borax or ammonia used to wash the grain surface of leather preparatory to applying dye solutions by hand or by machine; formerly a solution of stale urine.

Skin: The outer covering of a small animal; a small hide; among cattle hides, one weighing less than 15 lbs. in the green, salted state.

Skiver: The grain split of a sheepskin.

Slack tanned: Having an insufficient degree of tannage to produce the desired characteristics in a leather.

Slicker: A metal blade set in a wooden holder for setting out leather by hand.

Sling psychrometer: A portable, swinging pair of wet-and-dry-bulb thermometers for measuring the relative humidity of the atmosphere.

Slunk: The skin of an unborn or prematurely born animal.

Small-packer hide: The hide of an animal slaughtered, flayed and cured in one of the smaller packing plants with fewer facilities for specialization than are found in the big packing plants.

Snuffing: A very light buffing of the grain surface of leather.

Soak-fleshing: Fleshing hides during the preliminary soaking operation as distinct from fleshing after liming.

Soaking: Treating raw hides and skins with water to clean them, to remove salt and soluble matters and to permit them to absorb water to prepare them for the later operations.

Soap: A compound of alkali and fatty acid soluble in water and capable of emulsifying oils in water.

Soda ash: A white powder consisting of anhydrous sodium carbonate; an alkaline material used to neutralize acids and to clean and prepare vegetable-tanned leather for bleaching with acid.

Sodium bifluoride: A white salt used for disinfecting restricted-import hides and skins in accordance with the regulations of the Bureau of Animal Industry.

Sodium bisulfate: An acid salt sometimes used along with goulac in the oil wheel for filling and brightening the color of sole leather.

Sodium chloride: Common salt.

Sodium cyanide: An extremely poisonous material that has found some use as a powerful sharpening agent in lime liquors.

Sodium formate: A white crystalline salt soluble in water that forms complex compounds with chromic salts and is used in chrome tanning to bring about a greater degree of chrome tannage.

Sodium hydrosulfide: A sharpening agent used in liming that is just as effective, but less caustic in its action than sodium sulfide.

Sodium metaphosphate: A new tanning agent sold under the trade name of Calgon.

Sodium permanganate: A powerful oxidizing agent used in conjunction with sodium bisulfite and acid to whiten dirty raw stock.

Sodium sulfhydrate: Same as sodium hydrosulfide.

Sodium sulfide: A sharpening agent widely used in lime liquors, which forms both sodium hydrosulfide and caustic soda when dissolved in water.

Sodium tungstate: A white salt of tungsten used as a tanning agent in the manufacture of some kinds of white leather.

Solcod: Trade name for a group of commercial sulfonated cod oils.

Sol-Neats: Trade name for a series of commercial fatliquoring materials.

Sour dip: An acid solution containing Epsom salt and fermenting corn sugar into which dry sole leather is dipped to improve its color and feel before drying again.

Specific gravity: The weight of a substance per unit volume, recorded as the weight of a given volume of a substance divided by the weight of an equal volume of water.

Specific heat: The number of calories of heat required to raise the temperature of one gram of a material by 1° C.

Spent tan: Vegetable-tanning materials or solutions from which practically all of the tannin has been removed.

Spew: A portion of the oily constituents of leather that comes to the grain surface in the form of white crystallized fatty acids or as a gummy spew in the form of dark oxidized fatty acids.

Spirilla: Bacteria shaped like bent rods.

Splits: The layers of leather produced by splitting a hide or skin horizontally and designated as grain split, middle split and flesh split, according to location.

Splitter: A workman in a tannery who operates a splitting machine; a workman in a packing house who splits a carcass into two sides.

Splitting: Cutting a hide vertically with a knife into sides, bends, bellies, etc., or horizontally with a splitting machine into splits.

Splitting horse: A wooden frame for supporting a hide while cutting it into two sides.

Splitting machine: A machine equipped with gripping cylinders and a belt knife for cutting hides and skins horizontally into splits or for levelling the thickness of leather.

Sponging: Washing the grain surface of sole leather with an emulsion of kerosene, oils and waxes preparatory to rolling.

Spot hides: Hides sold for cash in the normal course of business without reference to the hide futures market.

Spray finishing: Applying liquid finishes to leather by means of a spray gun.

Spreading: The tendency for an oil to creep over the entire surface of water on which it is placed; important in stuffing leather and in oiling off.

Spready hide: A hide with a large area in relation to its weight.

Spruce extract: Trade name for a commercial vegetable-tanning extract made by acidifying and purifying sulfite liquors from paper mills.

Stag hide: The hide of a male of the ox kind that was castrated later in life than the steer, often when a year old. The longer castration is delayed, the more like a bull's the hide becomes. It has no recognized designation on the hide market, but is classed as steer or bull whichever it more nearly resembles, causing frequent difficulties in classification.

Staking: Flexing leather to separate fibers sticking together and thus to make it softer.

Staphylococci: Irregular clusters of spherical bacteria.

Steer hide: The hide of a male of the ox kind that was castrated when a calf several months old: it is finer, tighter in structure and more uniform in thickness than a bull hide.

Sticker: A butcher in a big packing plant who specializes in killing the animals by inserting his knife in the dewlap and severing the jugular vein.

Sticking piece: The dewlap or hanging skin under the throat of cattle, where the butcher first inserts his knife in the slaughter.

Stick vat: A vat containing vegetable-tan liquor into which calfskins are hung suspended from wooden sticks.

Stock liquor: Strengthening liquor; strong tan liquor used to strengthen liquors weakened by tanning stock in them.

Streptococci: Long chains of spherical bacteria.

Stretch of leather: The percentage increase in length of a strip of leather upon the application of a given pull in lbs. per unit area of cross-section of the strip.

Stuffing: Applying hot, molten greases to wet leather in a drum in the absence of water in excess of that held by the wet leather (about 50 percent by weight).

Sudoriferous glands: The sweat glands of the skin.

Suède leather: Very small skins finished on the flesh side by buffing to produce a fine and soft nap.

Sulfite cellulose: A by-product of paper mills produced in the sulfiting of wood pulp; used in vegetable tanning.

Sulfonated oils: Oils rendered soluble in water by chemical treatment with sulfuric acid.

Sulfur dioxide: A colorless gas of pungent and characteristic odor, made by burning pure sulfur in air; usually sold as liquid in steel tanks under pressure; used as reducing agent in making chrome liquor from sodium dichromate.

Sunning: The exposure of patent leather to strong sunlight to remove the tackiness from the varnish.

Superficial fascia: The flesh of a hide or skin.

Superspruce extract: Trade name for a highly purified form of spruce extract.

Surface tension: The tendency for the particles of a liquid to draw themselves together so as to present the smallest possible surface, as in the tendency for a drop of water to assume a spherical shape.

Swabbing: Spreading a liquid over the surface of leather by hand.

Sweat chamber: A warm room in which the hair of skins is loosened by bacterial decomposition.

Sweat glands: The glands of the skin just below the hair bulbs that secrete perspiration and pass it to the skin surface by means of ducts.

Sweating: An old method of loosening the hair of skins by allowing controlled putrefaction to take place in warm rooms.

Swelling: An increase in volume of protein fibers and jellies caused by absorption of water.

Synektan: Trade name for a series of commercial syntans.

Syntan: An artificial organic tanning material.

Synthesis: The building up of a substance from its simpler parts; the opposite of analysis.

Tacking: Stretching out a piece of damp leather and tacking it onto a wooden frame to dry in a smooth and stretched condition.

Tacky: Sticky, not slippery.

Tearing resistance: The load in lbs. required to continue a tear in leather once started.

Tail puller: A butcher in a big packing plant who specializes in skinning the tail of a carcass and pulling out the tail bone.

Tail vat: The tanning vat in a series that contains the weakest liquor; the vat into which the raw stock is hung for vegetable tanning.

Take-off: The flaying of an animal.

Tamol: Trade name for a neutral syntan sold in dry, granular form for producing a more uniform color in the dyeing of leather.

Tanasol: Trade name for a series of commercial syntans.

Tanigan: Trade name for a series of commercial syntans.

Tannin: A water-soluble material of vegetable origin that will combine with hide protein, rendering it resistant to putrefaction, and resist subsequent removal by washing.

Tanolin: Trade name for a series of commercial one-bath chrome-tanning materials; the original one-bath chrome liquor.

Tanoyl: Trade name for a series of commercial oil products used for fatliquoring and for various other treatments of leather.

Tare allowance: The portion of the total weight of a shipment of hides that represents weight other than that of the hides themselves and which is deducted from total weight in calculating the price to be paid.

Tartar emetic: Potassium antimony tartrate; used as a mordant in dyeing leather. Tawing: A name applied to alum tanning because the leather produced is not so stable as leathers produced by vegetable tanning or by chrome tanning.

Tempering: Soaking extracted vegetable-tanned sole leather in weaker tan liquors to remove the excess of tanning extract from the outer surfaces of the leather.

Temper of leather: The resistance of light leather to bending and the extent to which it recovers its shape after bending.

Tensile strength: The force required to pull apart a strip of leather per unit area of cross-section.

Tergitol: Trade name for a group of commercial wetting and penetrating agents.

Texas steer hide: A steer hide branded on side or butt, but of compact, narrow and close pattern and plump; not necessarily from Texas.

Thallophyta: The great division of plant life that includes bacteria, yeasts and molds.

Thermodynamics: Study of relations between heat energy and other forms of energy. Thermostat: A device for maintaining constant temperature.

Thermostat layer: The layer of hide or skin that contains the mechanism for controlling body temperature; the grain layer of leather.

Three-arm staker: A staking machine designed to stake fur skins with a very mild action.

Tin crystals: Stannous chloride or chloride of tin; a strongly acid material used as a mordant in dyeing leather.

Ti-pure: Trade name for a series of commercial titanium dioxide white pigments. Titanium dioxide: A pure white pigment used in white-leather finishes.

Titanox: Trade name for a series of commercial titanium dioxide white pigments.

Toggle: A metal clamp equipped with jaws to grip leather and a prong to hold it in place in a slotted metal frame.

Toggling: Stretching out a piece of damp leather and holding it in place for drying in a smooth and stretched condition by means of toggles set in slots in a metal frame.

Tooling: Producing patterns in relief on the grain surface of leather by hand with the aid of a hot metal tool; hand embossing.

Top finish: The last coat of finishing material applied in finishing leather.

Tragacanth: A gummy exudation from the stems of plants growing in various Asiatic countries and used as a plasticizer in leather finishes.

Tragasol: Trade name for a mucilagenous carbohydrate obtained commercially from the endosperm of certain vegetable seeds, such as the locust bean; incorporated into some types of leather to provide certain desirable characteristics; a plasticizer.

Triethanolamine: An organic liquid used with fatty acids to produce fine and stable emulsions of oils and waxes in water.

Trimming: Cutting away unwanted or unsightly parts of hides, skins or leather. Triton: Trade name for a series of commercial wetting, emulsifying and dispersing agents applicable in the treatment of raw skins and leather in the various processes of tanning, coloring and fatliquoring.

True skin: The derma or corium.

Trypsin: Enzymes obtained from the pancreas of an animal: pancreatin.

Twaddell hydrometer: An instrument for measuring the weight of a liquid per unit volume.

Two-bath process: A process in which raw stock is tanned by first treating it with a solution of sodium dichromate, which does not tan it, and then treating it with a reducing agent, such as hypo, to produce the basic chromic salt, which is the real tanning agent.

Unctuous: A term applied to leather with the soft, full, oily feeling of glove leather.
Urea: A substance abundant in perspiration; it is readily attacked by microörganisms with formation of ammonia compounds which sometimes destroy the
chrome-tanned leather in shoe uppers.

Vacuum evaporator: A device for removing water from tannin extracts and other solutions and concentrating them at lower temperatures by keeping the atmosphere above them at low pressure.

Varnish coat: The last coat of varnish applied in the finishing of patent leather.

Vat: A large rectangular container in which hides and skins are treated with water or water solutions, as in soaking, liming, bating, pickling and tanning; sometimes equipped with paddle wheels for agitating stock and liquor and sometimes with rocker frames as in the preliminary tanning of sole leather.

Vegetable tanning: The conversion of raw hides and skins into leather by treatment with water solutions of tannin extracted from materials of vegetable orgin.

Veiny leather: Leather in which the pattern of the larger blood vessels appears on the grain surface in the form of indentations.

Ventilating power: The ability of leather to pass water from an atmosphere of higher to one of lower relative humidity.

Vici kid: Trade name for a chrome-tanned glazed-kid leather; the first successful chrome-tanned leather.

Vinylite resin: Trade name for certain synthetic plastics used in leather finishes. Viscol: A vulcanized oil; an oil treated with sulfur monochloride to make it more plastic.

Voids: The percentage of the total volume of leather not occupied by leather fibers.

Warm-water pool: A vat of warm water in which sole-leather hides after liming are kept until ready to be unhaired.

Wart: A small fibroid tumor located in the grain layer of a skin; also a skin disease caused by a virus, or infective material.

Wear resistance: The reciprocal of the loss in thickness of leather after a definite amount of abrasive action on it.

Wet-and-dry-bulb thermometer: A device containing two thermometers, one with a dry bulb and the other with its bulb covered with a fabric soaked with water; when air is blown across the two bulbs, the wet-bulb thermometer will show a lower reading than the dry-bulb thermometer unless the air is saturated; from the two readings, the relative humidity of the air can be found in the relative-humidity tables.

Wetting agent: A material for treating dried chrome-tanned leather to facilitate its absorption of water to bring it back to the wet state.

Wheel: Same as drum.

Wheeling: Tumbling hides and skins or leather in a revolving drum.

Whitening: Buffing the grain surface of stuffed harness leather on a machine equipped with bladed cylinders.

Wild grain: Same as marbled grain.

Wool-clipping machine: A machine designed to clip the wool of shearlings and furs to any desired length.

Wool pullers: Those who specialize in dewooling sheepskins and preparing them for tanning or for sale to tanners.

Wringing: Removing the bulk of water from wet leather by passing it through specially designed wringers.

Yards: The department of a tannery in which hides and skins are tanned.

Yield of leather: The number of lbs. or sq. ft. of finished leather obtained from 100 lbs. purchased weight of raw stock.

Name Index

American Public Health Assoc., 200 American Soc. of Heating & Ventilating Engineers, 7, 555 American Tanning Extract Manufacturers' Assoc., 7, 280 Anderson, H., 701 Anderson, H. V., 58 Andres, C. A., 7, 18 Andress, J. C., 7 Ansul Chemical Co., 7, 366, 367 Apex Chemical Co., 7, 485, 599 Apostolo, C., 435 Argabrite, W. H., 7 Armour's Livestock Bureau, 7, 62, 63 Arny, L. W., 700 Astrom, A., 517 Atkin, W. R., 235, 410, 411, 700, 701 Atlas Refinery, Inc., 7 Aulson, P. G., 7 Aulson, P. G., 7 Aulson, P. G., 7 Aulson, P. G., 7 Austin, W. E., 516 Azemar, J., 235	Brown, F. L., 613 Brunner, R., 613 Bryant, A. W., 7 Buchanan, E. D., 189, 200, 457, 467 Buchanan, R. E., 189, 200, 457, 467 Burcke, G., 516 Bureau of Animal Industry, 7, 86, 96-107 Bureau of Foreign and Domestic Commerce, 7, 76, 280 Bureau of Standards, 7 Burfischer, W. C., 7 Bussino, G., 410 C Calco Chemical Co., Inc., 515 Calgon, Inc., 7, 422, 423, 484 Calver, S. W. 270 Cameron, D. H., 303, 409, 410 Carbide & Carbon Chemicals Corp., 7, 481, 507, 558 Carborundum Co., 7 Carlson, A. B., 7 Carlson, A. B., 7 Carter, Clyde, 7 Carus, E. H., 7 Carus, E. H., 7 Casaburi, V., 4355	Dempsey, M., 130 Dennis, Martin, 363 Dennis, Martin, 363 Dennis, Martin, 20., 7, 387-90, 395 Desmond, G. J., 7 Diener, E. J., 693-4, 702 Dietrich, H., 7 Dittmar, M. A., 7 Donnan, F. G., 516 Dow Chemical Co., 7, 466, 568, 592, 627 Downing, G. V., 702 Drueding Bros. Co., 7 Drueding, Caspar, 7 Dudycha, J. A., 7 Du Pont de Nemours, E. I. & Co., Inc., 7, 430, 486, 553 Durland, W. D., 280, 281, 304 E Eagan, F. W., 692 Eastman Kodak Co., 7, 177, 178 Edwards, R. S., 701 Effront, J., 259 Eisendrath, B. D. Tanning Co., 7, 173, 177, 182, 185, 215, 217, 370, 447, 449, 472, 473, 478, 520, 522, 525, 527, 558, 561.
Baer, J. B., 169 Bailey, O., 703 Releay Lorton Machine, Co., 7	Carter, Clyde, 7 Carus Chemical Co., Inc., 7 Caus, E. H., 7 Casaburi, V., 435 Caughley, F. G., 702 Central Scientific Co., 7 Chambard, P., 235, 409, 410, 432,	Eitner, W., 270, 435 Elliott, F. A., 200 Emley, W. E., 701 Endicott-Johnson Corp., 7, 171, 176, 180, 181, 227, 615, 616,
183, 467 Balanyi, D., 410 Balderston, L., 409, 516, 701 Baldwin, M. E., 395, 396, 397, 399, 409, 411 Barrett Co., 7 Bass, L. W., 410 Bassett, H., Jr., 409 Bear, A. W., 362	433, 435 Chantler, A. R., 7 Chapman, W. E., 613 Chater, W. J., 701 Chemical Solvents, Inc., 7 Chesley, K. G., 58 Church, M. B., 460, 463, 465-7 Churchill, J. B., 660, 701 Ciba Co., Inc., 7, 515	Eitner, W., 270, 435 Elliott, F. A., 200 Emley, W. E., 701 Endicott-Johnson Corp., 7, 171, 176, 180, 181, 227, 615, 616, 618, 619, 620 Engel, O., 270 Engelberg, H., 235 Enna, F. G. A., 436 Exans, John Sons, Inc., 7, 260 Evans, W. D., 7, 701 Everest, A. E., 516
Basert-Layon Machine Co., 7, 183, 467, Balanyi, D., 410 Balderston, L., 409, 516, 701 Baldwin, M. E., 395, 396, 397, 399, 409, 411 Barrett Co., 7 Bass, L. W., 410 Bassett, H., Jr., 409 Bear, A. W., 362 Beck, A. J., 702 Becker, F. H., 7 Becker, H., 259, 270 Becker, F. H., 259, 270 Becker, H., 259, 270 Becker, T., 259, 270 Becker, T., 259, 270 Becker, T., 259, 270 Becker, T., 702 Behr-Manning Corp., 7, 553, 554 Bell, K. E., 613 Benington, G. A., 7 Bergmann, M., 235, 701 Berkmann, J., 409 Bertram, O. W., 7, 510 Bianowitz, C. J., 7 Binney & Smith Co., 7	Clark, T. S., 7 Clark, W. M., 200 Clarke, I. D., 688, 701, 702 Clayton, W., 516 Clinton Co., 7 Cobb, R. M., 409 Coghill, D., 304 Colin-Russ, A., 304 Collett, R. L., 235 Commercial Solvents Corp., 7 Commodity Exchange, Inc., 7, 132-69 Commonwealth Color & Chemical Co., 7, 510	Falk, K. G., 270 Fink, H. J., 7 Fischer, E., 272 Fischer, H., 436 Fitzgerald, T. J., 7 Fladness, S. O., 7 Fleming, J. W., 205, 236, 270, 654 Fohr, F., 701 Foster, S. B., 74, 200, 399, 411, 436 Frey, R. W., 281, 304, 659, 688, 694, 701, 702

418

General Dyestuff Corp., 7, 389, 418

Gerngross, O., 436
Gerssen, J. N., 701
Gilbert, D. B., 703
Gillet, J. M., 7
Gillet, M., 613
Gilman, J. A., 360, 362
Givaudan-Delawanna, Inc., 591
Glass, I. R., 7, 76, 77
Gnamm, H., 516
Goeller, K. H., 223, 235
Goetz, A. W., 270, 410
Goldman, L., 235, 516
Goldman, L., 235, 516
Goldman, J. M., 517
Grasser, G., 436
Graham, J. M., 517
Grasser, G., 436
Grassman, W., 701
Graton & Knight Co., 662
Greef, R. W. & Co., Inc., 7
Greenleaf, L. S., Ir., 7
Greeves, W. S., 679, 701
Greilach, C., 7
Griliches, E., 436
Grimm, O., 410
Guettler, R. O., 702
Guillermond, A., 467
Gustavson, K. H., 409

Haas, Otto, 7 Hall Laboratories, Inc., 422, 424 Hamel, L. H., 7 Hamel, L. H., 7 Hamel, L. H. Leather Co., 7, 198, 224, 382, 482, 483, 554, 198, 224, 382, 483, 483, 534, 586
Hampshire, P., 234, 235
Hancock, F. H., 703
Handley, E. G., 701
Harmon, C., 7
Hart, J. M., 7
Hart, J. M., 7
Hart, J. M., 7
Hart, R. W., 688, 701, 702, 703
Hart, Wm., 7
Harvey, A., 304
Harvey, N. D., Jr., 235
Hauthaway, C. L. & Sons, 599, 600, 602-4
Heger, O., 701
Henry, W. C., 516
Hercules Powder Co., 7
Hertz, N., 701
Herzog, H. A., 434, 436
Hess, H., 436
Hey, A. M., 436 586

J

L

Laghloul, A., 436 Lamb, M. C., 410, 516, 613, 701 LaMotte Chemical Products Co., 7, 195, 196 LaMotte, F. L., 7 Lauffmann, R., 517 Law, D. J., 236, 271, 410 Lawrence, A. C. Leather Co., 662 Layton, H. B., 7

Freytag, H., 613
Fulton County Machine & Supply Co., Inc., 7, 441, 442, 443, 467, 552
Fuwa, T., 702

Gage, S. H., 58
Galaba, John, 7
Gallun, A. F., & Sons Corp., 7, 212, 215, 6219, 241, 307, 313, 315, 371, 448, 450, 471, 479, 568, 572, 581
Gallun, A. F., Jr., 7, 236, 256, 271, 313, 360, 362, 659, 671-2, 676, 680, 702
Gallun, E. A., 399, 411
Garz, J., 410
Gardinol Corp., 7
Garelli, F., 435
Gartenberg, H., 516
Gastellu, C., 436
Geib, M. N. V., 686, 688, 701
Geister, C. H., 7
General Dyestuff Corp., 7, 389, 418
Gerngross, Q., 436

Hide & Leather Publishing Co., Leather Manufacturer, 7, 20, 23, 31, 41-4, 48, 53
Ilide & Leather Publishing Co., Leather Manufacturer, 7, 20, 23, 31, 41-4, 48, 53
Ilide & Leather Publishing Co., Leather Manufacturer, 7, 20, 23, 31, 41-4, 48, 53
Ilide & Leather Publishing Co., Leather Manufacturer, 7, 20, 23, 31, 41-4, 48, 53
Ilide & Leather Publishing Co., Leather Manufacturer, 7, 20, 23, 31, 41-4, 48, 53
Ilide & Leather Publishing Co., Leather Manufacturer, 7, 20, 23, 31, 41-4, 48, 53
Ilide & Leather Publishing Co., Leather Manufacturer, 7, 20, 23, 31, 41-4, 48, 53
Ilide & Leather Publishing Co., Leather Manufacturer, 7, 20, 23, 31, 41-4, 48, 53
Ilide & Leather Publishing Co., Leather Manufacturer, 7, 20, 23, 31, 41-4, 48, 53
Ilide & Leather Publishing Co., 12, 48, 53
Ilide & Leather Publishing Co., 12, 48, 53
Ilide & Leather Publishing Co., 12, 448, 53
Ilide & Leather Publishing Co., 12, 48, 53
Ilide & Leather Publishing Co., 12, 48, 53
Ilide & Leather Publishing Co., 12, 42, 52
Lehm & Fink Products Corp., 7, 444, 45, 53
Ilide & Leather Publishing Co., 12, 446, 516, 516
Ilide & Leather Publishing Co., 12, 448, 53
Ilide & Leather Publishing Co., 12, 446, 516, 516
Ilide & Leather Publishing Co., 12, 446, 515
Ilide & Leather Publishing Co., 12, 446, 515
Ilide & Leather Publishing Co., 12, 466, 556
Ilide & Leather Publishing Co., 12, 466, 556
Ilide M., 7, 70
Ilide & Leather Publishing Co., 12, 466, 556
Ilide M., 7, 70
Ilide & Leather Publishing Co., 7, 444, 45, 51
Ilide & Leather Publishin

M

J
Jablonsky, L., 701
Jackson, D. D., 436
Jacoby, T. F., 410
Jettmar, J., 436
Johnson & Carlson, 7, 209
Johnson, George W., 7
Johnson, M., 436
Johnson, S. K., 7
Jungmann, J., 7

K
Kalb, G. H., 410
Kanagy, J. R., 701
Karlyn, M., 7
Kaye, M., 39, 58, 74, 235
Kelly, M. W., 58, 74, 348, 349, 350, 351, 354-6, 362, 399, 411, 419, 436
Kepec Chemical Corp., 7, 599, 603
Kern, E. J., 285, 292-3, 305, 346, 362, 411, 651, 655, 675, 700, 702
King, K. T., 7
Kinney, C. B., 363, 409, Kinzer, R., 409
Kinzer, R., 409
Kinzer, R., 409
Kinzer, R., 270
Koch, J. R., 270
Koch, J. R., 270
Kohn, S., 436
Koppenhoefer, R. M., 58, 236, 816
Krall, L., 246, 270
Krebs Pigment & Color Corp., 7
Kubeka, V., 701
Küntzel, A., 39, 58, 235, 270, 409

L
L
Laghloul, A., 446

McClure, H. B., 7
McPall, H. F., Jr., 7
McLoughlin, G. D., 7, 58, 69, 70, 74, 111, 129, 131, 200, 222, 236, 270, 516, 70
Marrian, T. H., 7
Maret, C. D., 7
Margee, G., 7
Margee, G McCandlish, D., 375, 410, 516, Monsanto Chemical Co., 7, 418, 466, 592, Moore, E. K., 236, 270, 516, 517 Morrison, C. S., 7 Morrison, W., 236 Mouries, M., 269, 270 Muller, R. G., 7 Mutual Chemical Co. of America, 7

National Aniline & Chemical Co., 7, 485

National Oil Products Co., 7, 430, 470, 473, 484, 486, 505, 621 Nelson, R. E., 7 Neun, D. E., 270 Newark Tanning Extract Corp., Niacet Chemicals Corp., 7 Niedercorn, J. G., 410, 436 Nihoul, E., 436 Northrop, J. H., 270

0

Oberfell, C. R., 7, 289 O'Flaherty, F., 7, 58, 111, 115-6, 119-24, 126, 130-1, 222, 236, 517 517
Ohio Leather Co., 7, 174-5, 182, 184, 218-9, 267, 369, 444, 449, 477, 521, 523-4, 526, 528, 548-9, 551, 573, 580, 582, 584-5, 599
Orth, F., 436
Orthmann, A. C., 7, 270, 410, 624, 628, 701
Otin, C., 410
Otto, G., 516, 701

P

P
Pacific Coast Borax Co., 7
Pacssler, J., 129, 282, 294, 304
Page, R. O., 292, 304, 360, 362
Page, W. J., 304
Paispearl Products, Inc., 7, 590
Pantaleoni, R., 7
Papayannis, A., 409, 410
Parker, J. G., 702
Partridge, E. P., 7, 424
Pawlowitsch, F., 702
Payne, M., 420, 436
Pearce, S. J., 7
Perkin, A. G., 516
Petrie, G. E., 7
Pfannmuller, J., 236
Philips, V., 270
Pickard, R. H., 702
Pierce Oil Products Corp., 7, 605
Pleass, W. B., 74, 236, 270, 420, 435
Pobl. W. 7 Pleass, W. B., 74, 230, 270, 420, 435
Pohl, W., 7
Popp, G., 259
Porter, R. E., 7, 362, 517, 702
Pototschnig, B., 270
Pouler, R., 410
Pound, T. I., 292, 293, 305
Powarnin, G., 702
Pratt Bros. Co., 7, 59, 64-6, 68, 73 Pratt, F. W., 7 Pratt, L. A., 7 Pratt's Reports, 59, 162 Price, J., Jr., 8, 59, 73-4, 134, Prien, H., 517 Procter, H. R., 200, 236, 305, 362, 410, 436, 628 Proctor & Schwartz, Inc., 8,

R

Special Equipment Co., 8, 541, 547
Reahl, J. J., 8
Reed-Blair Laboratories, 8
Rezebek, G., 236
Riess, C., 409, 517
Ringler, F. A. Co., 8, 577, 578
Roach, M. C., 8
Robertson, M. E., 58, 74, 130, 270
Robeson Process Co., 8, 283
Robinson, E. A., 8
Rockwell, G. E., 69, 74, 200, 222, 236
Roddy, W. T., 115, 116, 120, 122-4, 131, 236, 517
Rogers, A., 236, 305, 362, 517, 517
Rogers, A., 236, 305, 362, 517, 517
Rogers, F. A., 8
Rocker, J. K., 8
Spiers, C. H., 236, 702
Stather, F., 235, 236, 517
Stehling, Chas. H. Co., 8, 172, 179, 210-1, 217, 235, 268, 286, 308, 322, 329-35, 439-41, 443, 467, 472, 476, 487-9, 529, 572
Stehling, I. J., 8
Spiers, C. H., 236, 702
Stather, F., 235, 236, 517
Stehling, Chas. H. Co., 8, 172, 179, 210-1, 217, 235, 268, 286, 308, 322, 329-35, 439-41, 443, 457, 517
Stehling, Chas. H. Co., 8, 172, 179, 210-1, 217, 235, 268, 286, 308, 322, 329-35, 439-41, 443, 457, 517
Stehling, Chas. H. Co., 8, 172, 179, 210-1, 217, 235, 268, 286, 308, 322, 329-35, 439-41, 443, 467, 472, 476, 487-9, 529, 572
Stehling, Chas. H. Co., 8, 172, 179, 210-1, 217, 235, 268, 286, 308, 322, 329-35, 489-41, 443, 467, 472, 476, 487-9, 529, 572
Stehling, Chas. H. Co., 8, 172, 179, 210-1, 217, 235, 268, 286, 308, 322, 329-35, 489-41, 443, 457, 517
Stehling, Chas. H. Co., 8, 172, 179, 210-1, 217, 235, 268, 286, 308, 322, 329-35, 489-41, 447, 476, 472, 476, 487-9, 529, 572
Stehling, Chas. H. Co., 8, 172, 179, 210-1, 217, 235, 268, 286, 308, 322, 329-35, 489-41, 447, 472, 476, 487-9, 529, 572
Stehling, Chas. H. Co., 8, 172, 179, 210-1, 217, 235, 268, 286, 308, 322, 329-35, 489-41, 447, 476, 472, 476, 487-9, 529, 572
Stehling, Chas. H. Co., 8, 172, 179, 210-1, 217, 235, 268, 286, 308, 322, 329-35, 489-41, 447, 476, 472, 476, 487-9, 529, 572
Stehling, Chas. H. Co., 8, 172, 179, 210-1, 217, 235, 268, 286, 308, 322, 329-35, 489-41, 447, 476, 472, 476, 487-9, 529, 572
Stehling, Chas. H. Co., 8, 172, 179, 210-1, 217, 235, 268, 286, 308, 322, 329-35, 489-41, 447, 476, 472, 476, 487-9, 529, 572
Stehling, Chas. H. Co., 8, 172, 179, 210-1, 613, 628
Rogers, F. A., 8
Rogers, J. S., 269, 270
Röhm & Haas Co., 8, 228, 259, 270, 387, 414-5, 436, 483, 553, 594, 599, 600-5
Röhm, Otto, 3, 228, 236, 238-9, 259, 270, 420, 436, 517
Romer, E., 270
Rose, Henry, 8, 607
Rosenthal, G. J., 58, 270
Rosert, H., 436
Rothstein, H., 8
Rowe, F. M., 517
Rumpf, E. J., 8
Rundle, A. S. R., 703

Salcedo, I. S., 436
Salem Oil & Grease Co., 485
Salt, H., 516, 517
Sandoz Chemical Works, Inc., 8
Sauer, Arthur, 8
Saxe, Alexander, 8
Saxe Cutch Corp., 8
Saxe-Rushworth Co., 8, 389, 430, 485, 507, 509, 619
Saxe, Sig., 8
Schaffer, E. J., 436
Schiaparelli, C., 410
Schiller, B. A., 8
Schlichte, A. A., 236
Schmertz, J. R., 8
Schmelt, Armand, Inc., 8
Schneider, C., 8 Schmolt, J. A., S.
Schmolt, Armand, Inc., 8
Schneider, C., 8
Schroeder, L. E., 8
Schubert, A., 36, 613
Schultz, A., 363
Schultz, G. W., 305
Schwarz, R., 410
Seifriz, W., 517
Seitz, A., 58
Seiden, J. M., 8
Seldzer, J. M., 294, 305, 702
Serfass, E. J., 271, 410, 517
Seyewetz, A., 434, 436
Seymour-Jones, A., 39, 58, 236, 246
Seymour-Jones, F. L., 58, 271 Seymour-Jones, F. L., 58, 271, Proctor & Schwartz, Inc., 8, 410

S45-7

Pullman, E., 420, 436

Pullman, J., 420, 436

Q

Q

Quarck, R., 410

Queroix, M., 409, 436

Quinn, F. H., 292-3, 305

Quinn, J. W., 8

Quinn, L. M., 8

Quirin Leather Press Co., 8, 439, 467

Quirin, L. M., 8

Quortrup, R. C., 8

Seymour-Jones, F. L., 58, 271, 410

Shehee, S. L., 655

Sheppard, S. E., 8, 200

Sheridan, T. W. & C. B. Co., 8, 574, 575

Sherman, H. C., 270

Shillingford, J. T., 8

Shimidzu, M., 270

Shimidzu, M., 270

Shimidzu, M., 270

Shimidzu, M., 270

Shimington, R. M., 8

Simington, R. M., 8

Somerville, I. C., 436 Special Equipment Co., 8, 541,

Tanner, F. W., 467
Tanners' Council of America, 7, 8, 60, 76, 222
Tannin Corp., 8
Taylor Instrument Cos., 8, 264, 531-3, 540
Teas Extract Co., 8
Teas Inbin 8 Teas Extract Co., 8
Teas, John, 8
Teas, John, 8, 58, 69, 70, 74, 129, 200, 223, 236, 270-1, 410, 418, 420, 436, 517
Thom, C., 460, 463, 465-7
Thomas, A. W., 74, 200, 271, 273, 305, 345-51, 354-6, 361-2, 395-7, 399, 411, 419, 436, 517
Thompson, F. C., 235, 411, 700-1
Thuau, U. J., 236, 436, 702
Tiedemann, R., 8, 510
Tisdale, H. R., 8, 516
Titanium Pigment Corp., 8
Tupman Thurlow Co., Inc., 8
Turley, H. G., 7, 8, 39, 58, 236, 436 436 Turner, F. M., Jr., 517 Turner Tanning Machinery Co., 8, 221, 431, 440, 446, 467, 474-6, 481, 617, 621-2 Turney, Sir John, 238

United Fertilizer Co., 8 U. S. Industrial Chemicals, Inc.,

V

Vanderbilt, R. T. Co., 8 Van Valkenburgh, E. H., 8 Varo, W., 590-2, 669 Veitch, F. P., 659, 688, 694, 702 Victor Chemical Works, 8, 404 Vincent-Daviss, C. A., 8 Vogd, L., 8 Vogl, H., 409 Vollmar, C. J., 69, 74, 200 Von Stockar, W., 8, 272-3

Waigand, F., 701 Waldschmidt-Leitz, E., 271 Walker, H. B., 7, 8, 594 Wallace & Tiernan Co., Inc., 8, Wallace & Tiernan Co., In 190-1
Wallace, D., 8
Wallace, E. L., 362, 701-2
Wallerstein, Co., 259
Wallerstein, L., 236
Watson, J. C., 235
Webber, J. F., 8
Weidner, C. L., 410
Weil, Edmond, Inc., 8

Weinberger, E., 701
Wentworth, E. N., 8
White, E. W., 662
Whitmore, L. M., 688, 702-3
Widen, P. J., 409
Wiener, F., 436
Wilcox, W. H., 269, 271
Wilkens-Anderson Co., 8, 290
Willstaetter, R., 271
Wilson, F. H., 259, 270
Wilson, J. A., 58, 69, 74, 131, 168, 200, 231, 236, 248, 253, 256, 265, 271, 273, 285, 292-3, 305, 346, 360, 362, 372, 399, 410-1, 436-7, 456-9, 465-7, 493,

Subject Index

	ı	ì	ı	
4	ć	•	ì	

Abattoir, 705 Abies, tannin from various species of, 274 Abietic acid, 588 Abu-surug, tannin from, 277 Abu-surug, tannin from, 277

Acacia, tannin from various species of, 274

Acer, tannin from various species of, 274

Acer, tannin from various species of, 274

Acetic acid, in mordanting wood, 488

in vegetable-tanning extracts, 304

Acid dyes, 194, 478, 483, 511-15, 705

Acid destruction of leather, 694-700

Acidolene, 389, 390, 705

Acid swelling, guarding against, 336-7

Acids, in vegetable-tanning materials, 304 Acid swelling, guarding against, 336-7
Acids, in vegetable-tanning materials, 304
Acrylic aldehyde, 431
Acrylic-ester polymers, 595, 597
Aden, imports of raw stock from, 80-1
import restrictions, 106
Adipose tissue, 19, 34, 35, 45, 705
photomicrographs of, 35, 36, 45
Africa, import restrictions, 106
tannins from, 274-9
Age limitation of hides, 148
Air conditioning, 528, 705
Albino-rat skin, photomicrograph of grain Albino-rat skin, photomicrograph of grain pattern, 57 Alchornea triplinervia, tannin from, 274 Alcohol, 594, 598 Aldchyde tanning, 420-2 Aldehyde tanning, 420-2
Alder, tannin from, 274
Aleppo pine, tannin from, 277-8
Algarobilla, tannin from, 275-8
Algaria, imports of raw stock from, 80-2
import restrictions, 106
tannins from, 275, 278
Algin, use in leather finishes, 587
Alimu, tannin from, 279
Alizarine Orange (dye), 511
Alizarine Yellow (dye), 484
Alkali Green (dye), 512
Alkaline solution, 705
Alkanio, 705
Alliaptor leather, raw stock for, 167
Allophylus edulis, tannin from, 274
Almas, tannin from various species of, 27 Alnus, tannin from various species of, 274 Alphadinitrophenol, 194 Alphadinitrophenol, 194
Alpine Europe, tannins from, 277
Alternaria (molds), photomicrograph of, 465
Aluminum acetate, tanning with, 420
Aluminum chloride, tanning with, 419
Aluminum formate, tanning with, 420
Aluminum leaf, coating leather with, 606
Aluminum stearate, 607
Aluminum sulfate, in Calgon tanning, 429, 430
in dyeing leather, 478-9, 484
in treating sole leather, 619
tanning with, 386, 388, 418-20
Alum tanning, 418-20
Amaltas, tannin from, 275 Amaltas, tannin from, 275 American chestnut, tannin from, 275 Amla, tannin from, 277 Ammonia, use in dyeing leather, 473, 481, 484, 626 626
fatliquoring leather, 481, 486
leather finishes, 557
Amyl acetate, 594
Amylase, 242, 269, 463, 705
Anacardium occidentale, tannin from, 274
Analysis, 705

Ancient leather, 272-3 Andalusia, 53 Andalusia, 25
Anemometer, 539, 705
photograph of, 540
Angica, tannin from, 274
Angophora, tannin from various species of, 274
Anhydrous, 700
Anitics 500 Aniline, 588
Aniline dyes, 510-6, 591, 705
effect on ventilating properties of leather, 670
Aniline leathers, 565-6, 705 Anune leathers, 565-6, 705

Anogeissus, tannin from various species of, 274

Antelope leather, raw stock for, 167

Anti-blushing agents, 594, 705

Antiseptics, 189, 705

used in leather finishes, 591-3

Apis mellifica, 589

Apparent specific gravity of leather, 705

Appeal from determination of Hide Inspection

Bureau, 141

Apple tree, tannin from, 276 Bureau, 141
Apple tree, tannin from, 276
Apron leather, raw stock for, 167
Apuleia praecox, tannin from, 274
Arabia, import restrictions, 106
Aratiku gwazu, tannin from, 278
Arazym, 228, 705
Archeological discoveries of leather, 272
Arctostaphylos uva-ursi, tannin from, 274
Areca catechu, tannin from, 274
Areca catechu, tannin from, 274
Areolar tissue, 19, 35-6, 45, 705
photomicrographs of, 35, 36, 45
Areolar-tissue sheaths, 39, 705
Argentina, imports of raw stock from, 17, 18, 77-85
import restrictions, 106 import restrictions, tannins from, 274-80 Arkotan, 418, 705 Arsenic sulfide, use in unhairing, 222 Arsenic sulfide, use in unhairing, 222
Arteries, 34
Artificial gum, 588
Ash, 705
Asia, tannins from, 274-9
Aspergillus fiavus (molds), 465
fumigatus (molds), 465
niger (molds), 456-67
destruction of tannins by, 303
photomicrographs of, 456-64
terreus (molds), photomicrograph of, 465-6
Aspidosperma, tannin from various species of, 2674
274 Ass hides, imports of, 83 Assorting leathers, 451, 5 Astralagus gummifer, 587 Athlete's foot, 705 Atlasol, 705 Auramine (dye), 512, 515 Australia, imports of raw stock from, 77-85 tannins from, 274-8 Australian cherry, tannin from, 276 Autoclave, 705 Automobile leather, raw stock for, 167 Auxiliary unhairing cylinder, 451
Avicennia officinalis, tannin from, 274
Azo Yellow (dye), 512, 515

В

Babul, tannin from, 274
Bacillus, 188-9, 259, 269, 705
furfuris, 269
megaterium, 269
subtilis mesentericus, 259
Back, definition of, 615, 705

```
Back boarding, 705
Backers, 60-1, 705
Bacteria, 129-30, 186-91, 258-60, 705
hide damage by, 129-30
in bating, 258-60
in soaking, 186-91
method of reproduction, 188-9
photomicrographs of, 187-8
Bacterial counts, reduction by chlorination, 191
Badamier, tannin from, 279
Bag leather, chemical composition of, 643
fatiliquoring and dyeing, 485
import duties on, 87, 91
raw stock for, 167
                                                                                                                                                                                                                                                                                    Benzoun, 398
Benzopurpurine (dye), 515
Ber, tannin from, 279
B. erodiens, 259
Betanaphthol, 466, 591-2, 706
Betelnut palm, tannin from
                                                                                                                                                                                                                                                                                     Benzoin, 598
                                                                                                                                                                                                                                                                                    Betelnut palm, tannin from, 274
Betula alba, 598
                                                                                                                                                                                                                                                                                               tannin from, 275
                                                                                                                                                                                                                                                                                  tannin from, 275
Betula lenta, tannin from, 275
Big-packer hides, definition of, 17, 59, 706
Billfold leather, raw stock for, 167
Binders, 556-7, 566, 584-5, 595, 598, 706-7
Biobate, 259, 706
Birch oil, 16, 598
Bird leather, import duties on, 87, 92
Bismarck Brown (dye), 484, 513, 515
Bisulfiting vegetable-tanning extracts, 288, 706
Biting lice, 115
Black birch, tannin from, 275
Black cypress pine, tannin from, 275
    raw stock for, 167, 91 raw stock for, 167 strength, stretch and tearing resistance of, 664 Bagging of sole leather, 329 Bahau, tannin from, 275 Baldness 25
   Bahau, tannin from 270
Baldness, 25
Banksia, tannin from various species of, 274
Barbados, imports of raw stock from, 79-81
Barbatimao, tannin from, 278
Barbed-wire scratches, 108-9
Barium chloride, in making white leather, 388
Barium sulfate, oil-absorption value of, 590
                                                                                                                                                                                                                                                                                    Black birch, tannin from, 275
Black cypress pine, tannin from, 275
Black fox, import duties on, 86, 90
Black gum, tannin from, 276
Black locust, tannin from, 278
Black mallet, tannin from, 278
Black mangrove, tannin from, 277-8
Black oak, tannin from, 277-8
Black pine tannin from, 277-8
Black pine tannin from, 277-8
  Barium chloride, in making white leather, 388
Barium sulfate, oil-absorption value of, 590
Bark leather, 705
Bark salil, 329, 705
Barkometer, 286-7, 705
conversion tables, 288
temperature correction, 287
Barretan, 705
Baseball leather, alum-tanning of, 418-20
Calgon-tanning of, 429-30
finishing of, 605
plottomicrograph of, 634
tungstate-tanning of, 434
wear-resistance of, 690
Baseball-glove leather, dyeing and fatliquoring,
484-5
effect of splitting on tearing resistance. 654
                                                                                                                                                                                                                                                                                    Black pine, tannin from, 277
Black vegetable-tanned strap leather, finishing, 604
Black wattle, tannin from, 274
Blackheads, 30
                                                                                                                                                                                                                                                                                  Blacking harness leather, 626
Blacking machine, 550
Blackwood, tannin from, 274
Blanc fixe, oil-absorption values, 590
Bleached carnauba wax, 589
Bleaching machine, 617
permanganate, 454
sole leather, 617-8, 706
vegetable-tanned light leather, 452-6
wear-resistance of, 690
Baseball-glove leather, dyeing and fatliquoring,
484-5
effect of splitting on tearing resistance, 654
raw stock for, 167
Baseball-shoe upper leather (kangaroo), photo-
micrograph of, 642
properties of, 643, 664, 671, 674, 682, 684
raw stock for, 167
Basic dyes, 478-9, 511-3, 515, 706
Basicity of chromium salts, 364, 706
effect of temperature on, 408
Basil, 706
Basis grade of hides, 151, 706
Basis grade of hides, 151, 706
Basis grade of, 600, 605
import duties on, 87, 91
photomicrograph of, 633
properties of, 664
raw stock for, 167
Bate master, 237, 241
Bating, 237-71, 706
Baumé hydrometer, 288, 706
conversion tables, 288
Beam, 177, 216-9, 706
Beamhouse, 201, 706
Beamhouse, 201, 706
Beamhouse, 217
Beamster, 217, 706
Bearberry, tannin from, 274
Bearskin, photomicrograph of grain pattern, 57
Beaver (in packing house), 72, 706
Bedda, tanning from, 279
Beefwood, tannin from, 276
Beeswax, 589, 605, 706
Belgiam Congo, import restrictions, 106
imports of raw stock from, 18, 77-83
trade agreement, 89
Bellows leather, raw stock for, 167
Rallies definition of, 614, 706
                                                                                                                                                                                                                                                                                 sole leatner, 017-8, 700
vegetable-tanned light leather, 452-4, 706
Bleeding, 706
Blendoyl, 605, 706
Blood, used in leather finishes, 586, 605
Blood albumin, 585-6, 706
Blood vessels, 34
                                                                                                                                                                                                                                                                                    Bloodwood, tannin from, 276
Bloom, 706
                                                                                                                                                                                                                                                                                    Blue bush, tannin from, 274
                                                                                                                                                                                                                                                                                 Blue bush, tannin from, 274
Blue fig-bark, tannin from, 275
Blue-leaved mallet, tannin from, 276
Blushing, 594, 706
Boarding, 571-3, 601, 707
Boiling test for chrome leather, 369
Boils, 30
                                                                                                                                                                                                                                                                                Boils, 30
Bolivia, import restrictions, 106
imports of raw stock from, 77, 79, 80, 83, 85
tannins from, 275
Bombay, import restrictions, 106
imports of raw stock from, 18
Bookbinding leather, raw stock for, 167
Borax, in dyeing leather, 482, 484
fatliquoring leather, 478
leather finishes, 557
spaking raw stock 197
                                                                                                                                                                                                                                                                                  soaking raw stock, 197
Bordeaux (dye), 511, 515
                                                                                                                                                                                                                                                                                  Borneo cutch extract, see cutch extract
                                                                                                                                                                                                                                                                                 Boswellia serrata, tannin from, 275
Box myrtle, tannin from, 277
                                                                                                                                                                                                                                                                                Box myrtle, tannin from, 277
Box toes, import duties on, 86, 90
Boxing-glove leather, chemical composition of, 643
dyeing and fatiliquoring of, 483-4
photomicrograph of, 381
properties of, 664
raw stock for, 167
Brachysporium, 466
Bran drench, 268-70
Brand damage photographs of, 110
 imports of raw stock from, 10, //-os trade agreement, 89
Bellows leather, raw stock for, 167
Bellies, definition of, 614, 706
Belting leather, chemical composition of, 643
currying of, 627
effect of tanning and finishing on strength, 661-3
                                                                                                                                                                                                                                                                                 Brand damage, photographs of, 110
Branding, 108, 110-1
Brazil, import restrictions, 106
                                                                                                                                                                                                                                                                                imports of raw stock from, 77-85 tannins from, 274, 276-8, 284 trade agreement, 89 Brazil wax, 588
 import duties on, 86, 90
photomicrograph of, 632
properties of, 664
raw stock for, 167
Bend, definition of, 614, 706
                                                                                                                                                                                                                                                                                Break of leather, 564-5, 693, 707
method of measuring, 693
                                                                                                                                                                                                                                                                                Bridle leather, raw stock for, 167
Brief-case leather, raw stock for, 167
  Benzene, 594
```

5027201	11VDEX 751
Brilliant dyes, 511-5 Brining, 70, 707 Brisket, 707 Bristles, 55 British East Africa, import restrictions, 106 imports of raw stock from, 77-81, 85 British gum, 588 British Honduras, imports of raw stock from, 83, 84 British India, import restrictions, 106	California, tannins from, 274, 277-9 California laurel, tannin from, 279 Californ ides, 154 Call for hides, 154 Callitris, tannin from various species of, 275 Camellia thea, tannin from, 275 Calorie, 26-7, 707 Camanchile, tannin from, 277 Camel hide, grain pattern of, 57 Canada, imports of raw stock from, 18, 77-85 trade agreement, 89
British India, import restrictions, 106 imports of raw stock from, 18, 77-83 British Malaya, import restrictions, 106 imports of raw stock from, 82-3 British South Africa, import restrictions, 106 imports of raw stock from, 77, 84 British West Indies, imports of raw stock from, 80-1, 84 Brokers, hide, 133	Canaigre, tannin from, 278 Cancelled hide certificates, 143 Cancharana, tannin from, 275 Candelilla wax, 589, 707 Cap leather, raw stock for, 167 Caparossa, tannin from, 277 Cape Good Hope, import restrictions, 106 tannins from, 274, 277, 278
Brokers, fide, 133 Bromcresol Green, 194 Bromphenol Blue, 194 Bromthymol Blue, 194 Bruguiera, tannin from various species of, 275 Brush coat, 611, 707 Brushing leather, 555, 567-70, 622, 707	tannins from, 274, 277, 278 Cane sumac, tannin from, 277 Carapa moluccesis, tannin from, 275 Carbolic acid, 591 Carbon black, in linseed-oil varnishes, 610 Carding, 489, 707 machine, 489
Bromcresol Green, 194 Bromphenol Blue, 194 Bromphenol Blue, 194 Bruguiera, tannin from various species of, 275 Brush coat, 611, 707 Brushing leather, 555, 567-70, 622, 707 machines, 567, 622 Bryophyta, 187 Buck side leather buffing, 551 chemical composition of, 643 effect of relative humidity on area, 674 photomicrograph of, 640	Carisas spinarium, tannin from, 275 Carnauba wax, 481, 557, 561, 567, 588-9, 707 Carnauba-wax emulsion, 481 Carpincho skin, 707 Carragheein, 587 Casagha pine, tannin from, 275 Casagha tannin from, 275
photomicrograph of, 640 properties of, 664, 671, 674, 682, 684, 707 raw stock for, 167 Buffalo hides, imports of, 82 photomicrograph of, 630 Buffer, pH, 707 Buffing, 549-54, 625, 707 machines, 549, 551-4, 625	Cascalote, tannin from, 275 Case leather, fatliquoring and dyeing, 485 finishing, 604 import duties on, 87, 91 raw stock for, 167 Casein, effect on ventilating properties of leather,
raw stock for, 167 Buffalo hides, imports of, 82 photomicrograph of, 630 Buffer, pH, 707 Buffing, 549-54, 625, 707 machines, 549, 551-4, 625 Buffing suède leather, 485 Building a hide pack, 63-69, 707 Bulgaria, import restrictions, 106 imports of raw stock from, 77, 80-1 Bull hide, definition of, 16, 707 Bull oak, tannin from, 275 Bumelia obtusifolia, tannin from, 275 Bumelia obtusifolia, tannin from, 275 Bundling raw stock, 72-3 Bureau of Animal Industry, regulations, 97-107 Burna, imports of raw stock from, 77-8 tannins from, 275, 277, 279 Burnt sienna (pigment), 558 oil-absorption value of, 590 Bush mangrove, tannin from, 275 Bustanol, 594 Butcher cuts, 125, 707 photograph of, 125	use as binder in finishing, 556-7, 566, 584, 707 Cassia, tannin from various species of, 275 Castanea, tannin from various species of, 275, 281 Castanopsis, tannin from various species of, 275 Castile soap, 480, 566 Castor oil, 567, 594 Castration, effect on hides, 16
Bundling leather, 581-6 Bundling raw stock, 72-3 Bureau of Animal Industry, regulations, 97-107 Burma, imports of raw stock from, 77-8 tannins from, 275, 277, 279 Burnt sienna (pigment), 558 oil-absorption value of, 590	Castedine (dye), 514 Cattle hides, domestic production, 78 exports, 79 import duties on 86
Burnt umber (pigment), 558 oil-absorption value of, 590 Bush mangrove, tannin from, 275 Butanol, 594 Butcher cuts, 125, 707 photograph of, 125 Butt-branded hides, definition of, 17, 149, 707	imports, 77 movement into sight, 75 Caustic soda, destruction of hair by, 201 in Arazym unhairing, 229 in soaking dry stock, 196-9 CCCC dyes, 511-4 Ceanothus, velutina, tannin from, 275 Cedrillo tannin from, 275
Button lac, 588 Butyl acetate, 594 By-products, 235 Byrsonima, tannin from various species of, 275	Cedrillo, tannin from, 275 Celavinia, tannin from, 275 Celery-topped pine, tannin from, 277 Cellobiase, 463 Cells, epithelial, 21-3 reproduction of, 21 Cellulose ethers, 597 Cellulose pitrate, 593
Cabbage palmetto, tannin from, 278 Cabralea \$\$p., tannin from, 275 Cabretta, 52, 167, 707 photomicrograph of, 52 Caddie-bag leather, raw stock for, 167 Caesalpina, tannin from various species of, 275,	Cellulose nitrate, 593 Centigrade thermometer, 707 Central America, tannins from, 275, 284 Centrosome, 21 Ceratonia, siliqua, 587 Cerealin, 269 Ceriops, tannin from various species of, 275 Certification of hides, 140-2
284 Calcium chloride, use in unhairing, 229 Calcium hydrosulfide, as an unhairing agent, 209 Calcium hydroxide (see lime) Calco dyes, 515 Calfskins, photomicrographs of, 31-2, 35, 45-7, 56, 126-9, 202-5, 213-4, 245-6, 248, 318, 373, 426, 428-9, 454-5, 493-4, 542-4, 639	Ceylon, import restrictions, 106 tannins from, 279 Chalky carnauba wax, 589 Chamois leather, definition of, 16, 707 import duties on, 92 raw stock for, 167 tanning, 430-3
(see under all appropriate chapter headings) Calgon, 422-30, 484-5, 707 -chrome tanning, 430 leathers, photomicrographs of, 426, 428-9 tanning, 422-27 -vegetable-tanning, 427-30 white leathers, 429-30	Chamoising, 430-3, 707 Changes in import duties, 87, 96 Charges on hide contracts, 145 Checker, 581 Checking leather, 581-2, 584 Checking calfskins, 220, 707 machine, 221

```
Collagen, 30, 201, 207-31, 254-6, 708 action of enzymes on, 254-6 limewater on, 207-31
Collar leather, import duties on, 87, 91 raw stock for, 167
Collatone, 466, 556, 566, 592, 708
Collectors, hide, 132
Colloding, effect on ventilating
Chemical composition of leathers, 639-46, 686 at different depths below grain surface, 644 comparison of butts and bellies, 645 Chestnut blight, 281, 707 Chestnut oak, tannin from, 278 Chestnut-wood extract, acids in, 304
       cost of, 293
domestic consumption, 280
domestic production, 279
fixation value of, 298, 300
                                                                                                                                                                                                   Collodion, effect on ventilating properties of leather, 670
Colloidal clay, 389, 430, 485, 507-10, 619, 707 photomicrographs of, 509
       fixation value of, 298, 300 in dyeing, 516 penetrating power of, 298, 300 stability of, 294-6 sugars in, 304 tannin content, 292-3 at different Baume readings, 289
                                                                                                                                                                                                    Colombia, imports of raw stock from, 77-85
                                                                                                                                                                                                  trade agreement, 89
Colophony, 588, 607, 708
Color changes of dye pH indicators, 194
Color Index, 708
Color of bair, 25
 Chile, import restrictions, 106
imports of raw stock from, 80-1
tannins from, 275, 277
Chilson attachment for splitting machine, 446
                                                                                                                                                                                                    Color of hair, 25
                                                                                                                                                                                                           leather, effect upon temperature in sunlight, 693-4
                                                                                                                                                                                                   tannins, effect of pH value on, 301
Colorado steer hides, definition of, 16, 149, 708
Colored side leather, finishing, 602
Colorimetric measurement of pH value, 194-6
 China, import restrictions, 106
imports of raw stock from, 77-80, 82-3, 85
 imports of raw stock from, 77-8 Chinese nutralls, tannin from 272 Chinoline Yellow (dye), 512 Chloride ion, 192 Chlorinated rubber, 597 Chlorination, 191, 199 Chlorinator, photograph of, 190 Chlorine, 189-91, 466, 707 Chlorphenol Red, 194 Chocolate shade of leather, 481
                                                                                                                                                                                                   Colt hides, imports of, 83 photomicrograph of, 612 leather, properties of, 643, 664, 671, 674, 682, 684
                                                                                                                                                                                                   Comacid dyes, 511-4
Combined tannin, 296, 708
Combined water-soluble matter in leather, 292, 708
                                                                                                                                                                                                  Combined water-soluble matter in leather, 292, 70 Combing machine, 489 Commissions on hide contracts, 145 Commodity Exchange, Inc., hide by-laws, 139-54 hide rules, 154-9 photograph of trading on, 138 Common oak, tannin from, 278 Congo Red, 481 Conidia, 458, 466 Conidiophores, 458 Connective tissue, 19
 Chlorophenol Red, 194
Chocolate shade of leather, 481
Chondrus crispus, 587
Chosen, import restrictions, 106
Chromatin, 21
Chrome Blue Black (dye), 514
Chrome Brown (dye), 514
Chrome liquor, effect of variables on pH value, 395-9
                                                                                                                                                                                                Condiciphores, 458
Connective tissue, 19
Contract tanning, avoiding speculation by, 136
Contract tanning, avoiding speculation by, 136
Contract unit for hides, 152, 708
Conversion tables for specific gravity, degrees
Baumé, degrees Twaddell and degrees barkometer, 288
Copaifera lansdorii, tannin from, 275
Copernica cerifera, 589
Copperas, 481, 488, 626, 708
Cordoba, 53
Cordovan leather, 19, 53, 637, 708
chemical composition of, 643
photomicrograph of, 641
properties of, 664, 671, 674, 682, 684
raw stock for, 167
Coriaria, tannin from various species of, 275
Corium, 19, 708
Cork arm graining board, photograph of, 572
  manufacture of, 364-8
tanning with, 363-416
Chrome Red (dye), 511
Chrome retan cowhide leather, photomicrograph
of, 413
 chrome retanning, 412-4, 708
Chrome sole leather, 382-4, 623-4
photomicrograph of, 383
Chrome tanning, 363-416, 707
effect of added salts, 399-403
concentiation, 399
pH value, 401-3
temperature, 404-7
time, 404-7
   time, 404-7
Chrome Yellow (dye), 512
   (pigment), 590
Chrome-formate leathers, dyeing and fatliquoring,
                                                                                                                                                                                                   Cork arm graining board, photograph of, 572
Cork oak, tannin from, 278
    Chrome-formate tanning, 391-2
   Chrome Green (pigment), oil-absorption value of, 590
                                                                                                                                                                                                   Core dar, taning from, 278
Corn syrup, in making sole leather, 619-21
Correct pattern of hides, 59, 60, 708
Corrected grain, 708
Corylus avellana, tannin from, 275
Cost of vegetable-tunning materials, 293
Costa Rica, imports of raw stock from, 83-4
  Chromic oxide, 708
Chromic oxide, 708
Chromosome, 21
Chrysoidine (dye), 511, 515
Ciba dyes, 515
Citromyces, 463
City-butcher hides, definition of, 17, 59, 708
Civet 598
                                                                                                                                                                                                 Costa Rica, imports of raw stock from, 83-4 trade agreement, 89

Coulteria tinctoria, tannin from, 275

Counter leather, 19
import duties on, 86, 90
raw stock for, 167

Country hides, definition of, 17, 59, 708

Cowhides, photomicrographs of, 20, 23, 29, 40, 247, 377, 413, 610, 631, 633, 638, 640

Cow now, 122
    Civet, 598
 Civet, 598
Classification of hides, 16, 19, 149-51
Clearer-out, 60-1. 708
Cleistanthus collinus, tannin from, 275
Clipping machine, 488
wool skins, 487-8
Cloth Fast Blue (dye), 515
Cloth Red (dye), 515
Coast honeysuckle, tannin from, 274
Coccus, 188, 708
                                                                                                                                                                                                (see under all appropriate chapter hea
Cow pox, 122
Creosote, 591
Cresol Red, 194
Croccine Scarlet (dye), 484, 511
Crocking, 485, 708
Crop, definition of, 614, 708
Cropping, 614-5, 708
Cropsing, 614-5, 708
Crusting, 523, 708
Crusting, 523, 708
Crusting, 523, 708
Crusty break, 564, 585, 588, 709
Cryptomeria japonica, tannin from, 275
 Coccus, 188, 708
Coccus lacca, 588
Cochin China, import restrictions, 106
          tannins from, 276
  Cockle, 708
 Cocos romansoffiana, tannin from, 275
Cod oil, 482, 490, 619-20
 tanning with, 430-3
Cohesion of fibers, 492
Cold storage, photograph of calfskins in, 175
```

Cuba, imports of raw stock from, 77-8, 84 Cube gambier, 284
Cu-nao, tannin from, 275
Cupania, tannin from various species of, 275
Cure, standard of, 147
Curing, 62-70 Curic, Standard 01, 147
Curing, 62-70
damage, photomicrographs of, 126-9
shrinkage, 63-4, 69-70
Curly hair, cause of, 50
Currycomb scratches, photograph of, 109
Currying, 709
Curtidor, tannin from, 279
Curupy, tannin from, 274
Cutch extract, 282, 709
acids in, 304
cost of, 293
domestic consumption, 280
fixation value of, 298, 300
imports, 279
penetrating power of, 298, 300
stability of, 294-6
sugars in, 304
tannin content of, 292-3
at different Baumé readings, 289
Cuticle, 709
Cylinders for different type machines, photographs,
451-2
Cypress pine, tannin from, 275 Curing, 62-70 Cypress pine, tannin from, 275 Cypress wood, used in building vats and drums, 393 Cyprus, tannin from, 274 Czechoslovakia, import restrictions, 106 imports of raw stock from, 77, 78, 80, 82 trade agreement, 89

Dalbergia, tannin from, 275
Damage, hide, 108-131
Dampening chrome-tanned leather for staking, 521-3
Dandruff, 21
Danzig, import restrictions, 106
imports of raw stock from, 77, 79, 80
Dark-field illumination, 470, 709
Daub coat, 609, 709
Deacons, 709
Deacons, 709
Dealers, hide, 132-3
Deep yellow wood, tannin from, 278
Deerskins, imports of, 83
leather, chemical composition of, 643
properties of, 664, 671
raw stock for, 167
Degradation products, removal in bating, 242-4
Degreasing, 318, 386, 609, 709
Delayed curing, effects of, 69
Deliming, 239-40, 258
Deliverable grades of hides, 148-50
Delivery and payment for hides, 155
Delivery points for trading in hides, 154
Dematiaccae, 458, 466
Demodectic mange, 117-9
Dendryphium, 466
Denmark, import restrictions, 106
imports of raw stock from, 78-9, 83, 85 Demotectic marge, 1179
Dendryphium, 466
Denmark, import restrictions, 106
imports of raw stock from, 78-9, 83, 85
Derma, 19, 20, 23, 709
Deterioration of leather by acid, 694-700
Developed dyes, 485, 511-4, 709
Dewolaws, 61, 709
Dewolap, 60, 709
Dewooling, 70, 230-4
Dextrin, 588
Dhawa, tannin from, 274
Diacetone alcohol, 594
Diaphragm leather, raw stock for, 167
Diazine Black (dye), 485
Dibutyl phthalate, 594
Diethylene glycol, 558, 598-9, 605, 709
Differentials in hides, 152-3
Diluents, lacquer, 594
Dimensional changes in leather with relative humidity, 671-80
Dimethylamine, use in unhairing, 222, 709

Dinitrophenol, 194 Dinitrophenol, 194
Dioscorea atropurpurea, tannin from, 275
Diplococci, 189, 709
Direct dyes, 473, 481, 483, 511-5, 709
Directional ventilating power, 670-1, 709
Discoloration of tannin by iron, 304
Discount grades of hides, 152
Disease, hide damage by, 111-24
Disinfectant, 709
Disinfection of imported raw stock, 106 Disinfection of imported raw stock, 106 Disinfection of imported raw stock, 10 Disodium phosphate, 484 Dissolving hair, unhairing by, 229-30 Divi-divi, imports of, 279 stability of, 294 tannin from, 275, 284 use in dyeing, 516 Docks, tannin from, 278 Dog dung, use in bating, 237-8 Dogskins, import duties on, 86 Dolomite lime, 234 Domestic production of hides and skin Dolomite lime, 234
Domestic production of hides and skins, 75-77
vegetable-tanning extracts, 279
Dominican Republic, imports of raw stock from, 77, 78, 80
Doornbosch, tannin from, 274
Douglas fir, tannin from, 277
Dowicides, 466, 592, 709
Drawn flanks, 709
Drenching, 268-70, 709
Dribrite binder, 602-3
Drier, linseed-oil, 609
Drums setting-out machine, 440, 476
Drums, photographs of, 179-81, 219, 378, 392-4, 481-2
Drumhead leather, raw stock for. 167 481-2
Drumhead leather, raw stock for, 167
Drumning, 709
Dry dip for sole leather, 622-3, 709
Dry lides, 17, 196, 199
Dry loft, 471, 709
Dry milling, 316, 710
Dry, salted hides, 17, 72
Drying light leathers, 518-55
heavy leathers, 620-1, 626
raw stock, 71 raw stock, 71
distortions during, 177-8
tunnels, 519-20, 545-8, 559, 709
Dubbin, 710
Duponol, 553, 710
Dusting, 710
Duties, import, 86-96
Dye indicators for measuring pH value, 194, 710
Dyeing light leathers, 473, 509
Dyestuffs, aniline, 510-6, 591, 705
natural, 715 raw stock, 71

E
East Africa, import restrictions, 106
tannins from, 275
East India kips, 18
East Indies, tannins from, 277, 284
Ecuador, import restrictions, 106
imports of raw stock from, 80-1, 83, 85
trade agreement, 89
Egg albumin, 566, 585, 710
Egg yolk, 478-501, 710
effect on fatliquoring, 502-5
photomicrograph of fatliquor, 503
Egypt, import restrictions, 106
imports of raw stock from, 80-2
Elacocarpus grandis, tannin from, 275
Elastin, 36, 710
action of limewater on, 202-5
Elastin fibers, hydrolysis of, 202-5, 245-54
photomicrographs of, 202-5, 245-50
Electrometric measurement of pH value, 290
Elephant roots, tannin from, 275
Elephantorrhiza burchellii, tannin from, 275
Elk hides, imports of, 83
Elk-leather fatliquor, 480
fatliquoring, 480
fatliquoring, 480
finishing, 600, 603 fatliquoring, 480 finishing, 600, 603 raw stock for, 167 properties of, 643, 664 Embossed leathers, designs for, 577

```
Back boarding, 705
Backers, 60-1, 705
Bacteria, 129-30, 186-91, 258-60, 705
hide damage by, 129-30
in bating, 258-60
is accepting 196 01
                                                                                                                                                                                                                   Benzoin, 598
                                                                                                                                                                                                                  Benzopurpurine (dye), 515
Ber, tannin from, 279
B. erodiens, 259
Betanaphthol, 466, 591-2, 706
                                                                                                                                                                                                               Betanaphthol, 466, 591-2, 706
Betelnat palm, tannin from, 274
Betula alba, 598
tannin from, 275
Betula lenta, tannin from, 275
Big-packer hides, definition of, 17, 59, 706
Bilfold leather, raw stock for, 167
Binders, 556-7, 566, 584-5, 595, 598, 706-7
Biobate, 259, 706
Birch oil, 16, 598
Bird leather, import duties on, 87, 92
Bismarck Brown (dye), 484, 513, 515
Bisulfiting vegetable-tanning extracts, 288, 706
Biting lice, 115
Black birch, tannin from, 275
Black cypress pine, tannin from, 275
Black gum, tannin from, 276
Black locust, tannin from, 276
Black mallet, tannin from, 276
Black mallet, tannin from, 276
Black mallet, tannin from, 276
Black oak, tannin from, 276
Black oak, tannin from, 277
Black oak, tannin from, 277-8
Black pine, tannin from, 277-8
Black pine, tannin from, 277-8
Black pine, tannin from, 277-8
Black pretable-tanned strap leather, finishing, 60.
          in soaking, 186-91
method of reproduction, 188-9
photomicrographs of, 187-8
   Bacterial counts, reduction by chlorination, 191 Badamier, tannin from, 279
   Bag leather, chemical composition of, 643 fatliquoring and dyeing, 485 import duties on, 87, 91
           raw stock for, 167
   strength, stretch and tearing resistance of, 664
Bagging of sole leather, 329
Bahau, tannin from, 275
   Baldness, 25
Banksia, tannin from various species of, 274
Barbados, imports of raw stock from, 79-81
Barbatimao, tannin from, 278
Barbed-wire scratches, 108-9
     Barium chloride, in making white leather, 388
   Barium chloride, in laking white feather, 18 Barium sulfate, oil labsorption value of, 590 Bark leather, 705 Bark mill, 329, 705 Barkometer, 286-7, 705 conversion tables, 288
                                                                                                                                                                                                                 Black pine, tannin from, 27/-8
Black pine, tannin from, 277
Black vegetable-tanned strap leather, finishing, 604
Black wattle, tannin from, 274
Blackheads, 30
Blacking harness leather, 626
Blacking parching, 550
           temperature correction, 287
   Barretan, 705
Baseball leather, alum-tanning of, 418-20
                                                                                                                                                                                                               Blacking harness leather, 626
Blacking machine, 550
Blackwood, tannin from, 274
Blanc fixe, oil-absorption values, 590
Bleached carnauba wax, 589
Bleaching machine, 617
permanganate, 454
sole leather, 617-8, 706
vegetable-tanned light leather, 452-4, 706
Bleeding, 706
Bleeding, 706
Blendoyl, 605, 706
Blood, used in leather finishes, 586, 605
Blood vessels, 34
Bloodwood, tannin from, 276
  Baseball learner, alum-tanning or, 418-20
Calgon-tanning of, 429-30
finishing of, 605
photomicrograph of, 634
tungstate-tanning of, 434
wear-resistance of, 690
Baseball-glove leather, dyeing and fatliquoring,
                            484-5
           effect of splitting on tearing resistance, 654 raw stock for, 167
  raw stock for, 167
Baseball-shoe upper leather (kangaroo), photomicrograph of, 642
properties of, 643, 664, 671, 674, 682, 684
raw stock for, 167
Basic dyes, 478-9, 511-3, 515, 706
Basicity of chromium salts, 364, 706
effect of temperature on, 408
Basil, 706
Basis grade of hides 151, 706
                                                                                                                                                                                                                 Bloodwood, tannin from, 276
Bloom, 706
                                                                                                                                                                                                               Bioom, 706
Blue bush, tannin from, 274
Blue fig-bark, tannin from, 275
Blue-leaved mallet, tannin from, 276
Blushing, 594, 706
Boarding, 571-3, 601, 707
Boiling test for chrome leather, 369
Boils, 30
Boilva import restrictions, 106
  Basis grade of hides, 151, 706
Basketball leathers, chemical composition of, 643
finishing of, 600, 605
import duties on, 87, 91
photomicrograph of, 633
  properties of, 664
raw stock for, 167
Bate master, 237, 241
Bating, 237-71, 706
Bauhinia vahii, tannin from, 275
                                                                                                                                                                                                                Bolivia, import restrictions, 106
imports of raw stock from, 77, 79, 80, 83, 85
tannins from, 275
Bombay, import restrictions, 106
                                                                                                                                                                                                               Bombay, import restrictions, 106
imports of raw stock from, 18
Bookbinding leather, raw stock for, 167
Borax, in dyeing leather, 482, 484
fatliquoring leather, 478
leather finishes, 557
soaking raw stock, 197
Bordeaux (dye), 511, 515
Borneo cutch extract, see cutch extract
Boswellia serrata, tannin from, 275
Box myrtle, tannin from, 277
Box toes, import duties on, 86, 90
Boxing-glove leather, chemical composition of, 643
dyeing and fatliquoring of, 483-4
photomicrograph of, 381
properties of, 664
  Baumé hydrometer, 288, 706
conversion tables, 288
Beam, 177, 216-9, 706
Beamhouse, 201, 706
Beam knife, 217
Beamster, 217, 706
   Bearberry, tannin from, 274
   Bearskin, photomicrograph of grain pattern, 57
Beaver (in packing house), 72, 706
   Bedda, tanning from, 279
  Beefix anning from, 279
Beefixood, tannin from, 276
Beeswax, 589, 605, 706
Belgian Congo, import restrictions, 106
imports of raw stock from, 85
Belgium, import restrictions, 106
imports of raw stock from 18, 77, 82
                                                                                                                                                                                                               photomicrograph ot, 381
properties of, 664
raw stock for, 167
Brachysporium, 466
Bran drench, 268-70
Brand damage, photographs of, 110
Branding, 108, 110-1
Brazil, import restrictions, 106
imports of raw stock from, 77.85
          imports of raw stock from, 18, 77-83
imports of raw stock from, 18, 77-83 trade agreement, 89
Bellows leather, raw stock for, 167
Bellies, definition of, 614, 706
Belting leather, chemical composition of, 643 currying of, 627
effect of tanning and finishing on strength, 661-3 import duties on, 86, 90
photomicrograph of, 632
properties of, 664
raw stock for, 167
Bend, definition of, 614, 706
Benzene, 594
                                                                                                                                                                                                                       imports of raw stock from, 77-85 tannins from, 274, 276-8, 284 trade agreement, 89
                                                                                                                                                                                                               Brazil wax, 588
                                                                                                                                                                                                               Break of leather, 564-5, 693, 707
method of measuring, 693
                                                                                                                                                                                                               Bridle leather, raw stock for, 167
Brief-case leather, raw stock for, 167
Benzene, 594
```

Gambier extract, cost of, 293 imports of, 279 tannin content of, 292-3 use in dyeing, 478, 483, 516 Gamble of hide-price fluctuation, avoiding, 161-5 Gamma-dinitrophenol, 194 Ganib, tannin from, 276 Garcinia mangostana, tannin from, 276 Gardinol, 430, 485-6, 553, 712 Garment leather, chemical composition of, 643 dyeing and fatliquoring, 484 finishing, 602, 604 import duties on, 86-7, 91-2 photomicrograph of, 635 properties of, 664, 671 raw stock for, 167 Garnet lac, 588 Gasket leather, chemical composition of, 643 raw stock for, 167 Gauge, thickness, Randall & Stickney, 357 Turner, 446	Grain staking, 526 Grain surface, 31, 39 photomicrograph of, 31 Graining leather, 571-3, 601, 712 Grainy leather, 37, 240-2, 712 Grasers, 712 Gray hair, cause of, 25 Great Britain, import restrictions, 106 Greece, import restrictions, 106 imports of raw stock from, 82 Green and green, salted stock, 15 Green wattle, tannin from, 274 Grevillia striata, tannin from, 276 Grey alder, tannin from, 276 Grub damage, photographs of, 111-4 Grubby hides, 712 Grubs, 111-5 Guaiac, tannin from, 274 Guaiac, tannin from, 274 Guaiac, tannin from, 274 Guaine, 590 Guara, tannin from, 276 7
Garnet lac, 588 Gasket leather chemical composition of 643	Grubby hides, 712 Grubs 111-5
raw stock for, 167	Guaiac, tannin from, 274
Wohurn 579	Guanine, 590 Guara, tannin from, 276-7 Guatemala, imports of raw stock from, 83
Gear leather, raw stock for, 167 Gelatin, 30, 712	Guatemala, imports of raw stock from, 83 trade agreement, 89 Guinea Green (dye), 512
diffusion of tannin into, 344-7	Guinea-pig skin, grain pattern of, 57
diffusion of tannin into, 344-7 distortion on drying, 177-8 effect on ventilating power of leather, 670 in leather finishes, 566, 586, 607	Gully ash, tannin from, 276
effect on ventilating power of leather, 670	Gum arabic, effect on ventilating properties of leather, 670 Gums used in leather finishes, 586-8
	Gums used in leather finishes, 586-8
Germany, import restrictions, 106	Gummy spews, 490
Germany, import restrictions, 106 imports of raw stock from, 77, 79, 80, 81, 83 Gie-bob, tannin from, 278 Gie-gay, tannin from, 278	Gun-metal side leather, finishing, 603
Gie-gay, tannin from, 275	Gusset leather, raw stock for, 168 Guyacan, tannin from, 275
Gie-quang, tannin 110m, 270	
Gimlet, tannin from, 276 Glands, 25	H
Glass electrode, 290, 712	Hagalay, tannin from, 275
Glass electrode, 290, 712 Glassy layer, 53, 712 Glauber's salt, 712	Hair, 21
effect on, chrome tanning, 397-8, 401	Hair, 21 action of caustic soda on, 207 limewater on, 206, 208, 231 sulfides on, 207
effect on, chrome tanning, 397-8, 401 tannin fixation, 356-7 in Arazym unhairing, 229	sulfides on, 207
in Arazym unhairing, 229 in making white leather, 388-9 Glazed kid leather, finishing, 600-1 raw stock for, 167 Glazing, 560-1, 565, 609, 712 effect on ventilating power of leather, 670 Glazing jack, 560, 565, 609, 712 Glazing lacquer, 594 Glossarv of terms, 705-24	Hair follicle. 21-3. 116-20
Glazed kid leather, finishing, 600-1	Hair papilla, photomicrograph of, 23 Hair slips, 712
raw stock for, 167	Hair slips, 712 Hair-washing machine, 235
effect on ventilating power of leather, 670	Hair-washing machine, 235 Hairy leather, chemical composition of, 643
Glazing jack, 560, 565, 609, 712	
Glazing lacquer, 594	raw stock for, 168
Glossary of terms, 705-24 Glove leathers, chemical composition of, 643	photomicrograph of, 529 properties of, 664 raw stock for, 168 Haiti, imports of raw stock from, 80-1 trade agreement, 89 Hakea, tannin from various species of, 276 Hand graining, 571-3, 601 Hand plunger, photograph of, 211 Hand setting, 478 Hand slicker, 476
dyeing and fatliquoring, 484-5	Hakea, tannin from various species of, 276
photomicrograph of 638	Hand graining, 571-3, 601
properties of, 654, 664	Hand plunger, photograph of, 211 Hand setting, 478
raw stock for, 167	Hand slicker, 476
Glyceride, 490	Hand swabbing, 558 Handbag leather, raw stock for, 168
Glossary of terms, 705-24 Glove leathers, chemical composition of, 643 dyeing and fatilquoring, 484-5 import duties on, 87, 91-2 photomicrograph of, 638 properties of, 654, 664 raw stock for, 167 Glue stock, 712 Glyceride, 490 Glycerin, in finishing, 606 oiling off, 483 Glyco Neats, 712 Goatskins, photomicrographs of, 51, 380, 611	Hand swabbing, 558 Handbag leather, raw stock for, 168 Handler vats, 309, 316, 712 Hannoki, tannin from, 274 Harness leather, 624-6 chemical composition, 643-4
Glyco Neats, 712	Hannoki, tannin from, 274 Harness leather 624-6
Glyco Neats, 712 Goatskins, photomicrographs of, 51, 380, 611 (see under all appropriate chapter headings) Gold finishes, 590 Gold leaf, applying to leather, 606-9 Gold-beaters' skin, 168, 712 Golden wattle, tannin from, 274 Golf-grip leather, finishing, 588, 605 raw stock for, 167 Gommeline, 588 Goose pimples, 27	chemical composition, 643-4 import duties on, 86, 90
(see under all appropriate chapter headings) Gold finishes, 590	import duties on, 86, 90
Gold leaf, applying to leather, 606-9	photomicrograph of, 626 properties of, 664, 671 raw stock for, 168 Hat sweatband leather, finishing, 602,
Golden wattle tannin from 274	raw stock for, 168
Golf-grip leather, finishing, 588, 605	raw stock for. 168
raw stock for, 167	Hawaii, tannins from, 274
Goose pimples. 27	raw stock for, 168 Hawaii, tannins from, 274 Hazel, tannin from, 275 Head, definition of, 614, 712 Head splitting, 712
Goran, tannin from, 275	Head splitting, 712
Goose pimples, 27 Goran, tannin from, 275 Gothar, tannin from, 279 Goulac, 283, 619-20, 712 Grades of hides deliverable at basis price, 152 Grading and warehousing for hides committee	Head vat, 712 Headers, 60-1, 712 Headless shoulder, 614 Heater for tan liquors, 335
Grades of hides deliverable at basis price, 152	Headless shoulder, 614
	Heater for tan liquors, 335 Heath honeysuckle tannin from 274
on, 139 Grading of leather, 579-80 Grain cracking, resistance of leather to, 664, 691 Grain cracks from improper flaying, photograph	Heavy hides, definition of, 16, 149-50, 712
Grain cracks from improper flaving photograph	Heavy leathers, finishing, 614-28
cram cracks from unproper maying, photograph	Hadging avoiding energiation by 137 712
of, 126 Grain layer, 25, 712 Grain patterns, 55, 8, 712	Heater for tan liquors, 335 Heath honeysuckle, tannin from, 274 Heavy hides, definition of, 16, 149-50, 712 Heavy leathers, finishing, 614-28 Hedging, avoiding speculation by, 137, 712 Heifer, 712 Hematine, 473, 483, 713 Hemlock, tannin from 274, 279, 284

TT 1 1 1 1 1 1 1 1 1 204	Hyd
Hemlock-bark extract, acids in, 304	LLyu.
cost of, 293	Hyd
domestic consumption, 280	Hyd
fixation value of 298	Hyd
imports, 279	Hyg
domestic consumption, 280 production, 279 fixation value of, 298 imports, 279 penetrating power of, 298 stability of, 294-6 sugars in, 304 tannin content of, 292-3 at different Baumé readings, 289 use in dyeing, 516	Нур
stability of, 294-6	Hyp
sugars in, 304	Hyp
tannin content of, 292-3	Hyp
at different Baumé readings, 289	
at different Balline Featings, 267 use in dyeing, 516 Hen manure, use in bating, 237-8 Heritiera fomes, tannin from, 276 Herpes, 123 Hickory wattle, tannin from, 274 Hides definition of 15, 713	
Hen manure, use in bating, 237-8	T1 -
Herber 122	Icela
Hickory wattle tannin from 274	Impi
Hides definition of 15 713	1mpc Impc
Hides, definition of, 15, 713 nomenclature of, 16	Impo
preparation for market, 59-74	ve
(see under appropriate chapter headings) Hide By-laws, 139-54 Hide certificates, 142-3	Inco
Hide By-laws, 139-54	me
Hide certificates, 142-3	India
Hide contract for future delivery, 143, 146, 156,	im
157	tar
Hide damage, 108-31 Hide Exchange, 138	tar
Hide fibers growth of 30	India
Hide fibers, growth of, 30 Hide house, 170-6	ph Tudic
photographs of, 174-6	India India
photographs of, 174-6 Hide Inspection Bureau, 141-3 Hide market, variations in, 134-6, 160, 164	im
Hide market, variations in, 134-6, 160, 164	Indig
Hide pack, 63-9 Hide rules, 154-9	Indo
Hide rules, 154-9	tar
Hide spreaders, 64, 67, 713	Indu
Hide spreaders, 64, 67, 713 Hide stamping machine, 172 Hide trade committees, 139	Infe
Hide trade committees, 139	Inga
Hide-droppers, 60-1, 713	Ingu
Hide-marking hammer, 172	Inne
Hides and skins as by-products of packing	Insol
industry, 15, 19	Inspe
Hide trade committees, 139 Hide trading ring, photograph of, 138 Hide-droppers, 60-1, 713 Hide-marking hammer, 172 Hides and skins as by-products of packing industry, 15, 19 Hide-substance content of pickled stock, measurement of, 372-4 Highland oak, tannin from, 278 Hill oak, tannin from, 278 Himalayan maple, tannin from, 274	Inspe Inspe
Highland oak tannin from 279	Inter
Hill oak tannin from 278	Inula
Himalayan maple, tannin from, 274	Inve
Hind-leggers, 61, 713	Įon,
Himalayan maple, tannin from, 274 Hind-leggers, 61, 713 Histology of hides and skins, 19-58	loniz
Hog pox, photographs of damage by, 122	Iran,
Hog pox, photographs of damage by, 122 Hogskins, photomicrographs of, 24, 54, 119, 122,	Iraq,
250, 321 (see under appropriate chapter headings) Hog strips, 19, 77-8 Honduras, imports of raw stock from, 77, 79, 80, 83-5	im
Hog strips, 19, 77-8	Iride
Honduras, imports of raw stock from, 77, 79, 80.	Irish
83-5	
trade agreement, 89 Hong Kong, import restrictions, 106 imports of raw stock from, 83	Įrish
Hong Kong, import restrictions, 106	Iron
imports of raw stock from, 83	Iron Iron
Hopea, tannin from various species of, 276 Horned-toad skin, grain pattern of, 57 Horse mortality, 78	Iron
Horse mortality 78	Ironi
Horse mortality, 78 Horse, wooden, 268, 713 Horse, who work the second of 52, 56, 2412	Trony
Horsehides, photomicrographs of, 53, 56, 341-2.	Ising
Horsehides, photomicrographs of, 53, 56, 341-2, 384-5, 612, 634, 641 (see under appropriate chapter headings)	Italia
(see under appropriate chapter headings)	im
	Italy
Hot-air stuffing mill, 481, 713 Hot water, resistance of leather to, 369, 418, 421-2, 432, 692, 719	im tar
421-2 432 602 710	Itcha
riuman skin, photomicrographs of, 22, 26, 28,	
36 38	
Humidiguide, 532	_
Hungary, import restrictions, 106	Jama
Hunting-boot leather, ventilating power of, 671 Hyaline layer, 39, 713	Tow-1
Hybrids, 52	Jamb
Hydnora longicollis, tannin from, 276	Jamr Janu
Hydraphtal, 713	Japan
Hydraphtal, 713 Hydrated lime, 234	Japai
Hydraulic leather, raw stock for, 168	Japan
Hydraulic leather, raw stock for, 168 Hydraulic press, 173	Japai
Hydrochloric acid, destructive action on leather.	Japai
698-9	Japai
effect on plumping, 358	Japan
in chrome tanning, 379	lava

Hydrochloric acid, in drenching, 270 dyeing, 485
Hydrogen ion, 192-4
Hydrolysis, 189, 201, 205, 245-59, 713
Hydroxide ion, 192-3
Hygrometer, 532-3, 713
Hypernic, 480-1, 484, 516, 713
Hypha, 457
Hypo, 363, 388, 713
Hypoderma bovis, 111-2

I

and moss, 587 inge Aire Pasting Dryer units, 545-7 ort duties, 86-96 ort restrictions from various countries, 106 orts of raw stock, 75-85 getable-tanning materials, 279 mel drums, 392-4 etal, 713 etal, 713
a, import restrictions, 106
aports of raw stock from, 77-85
anage, 18, 713
nnins from, 274-9, 282
an buffalo hides, imports of, 82
an Red (pigment), 558, 590
a-tanned hides, 18
a-tanned hides, 18
a-tanned hides, 18 port duties on, gotine (dye), 513 schina, import restrictions, 106 nnins from, 275, 278 sline (dye), 513 ction, 713 , tannin from various species of, 276-7 ia gwazu, tannin from, 276 r soles, import duties on, 86, 90 le leather, raw stock for, 168 ection, grading and weighing of hides, 142 ection of hides at tannery, 170 ector-in-chief for hides, 140 rnational Critical Tables, 273, 631 ase, 463 rtase, 463 713 zation, 192-3
a, import restrictions, 106
aports of raw stock from, 80-2
b, import restrictions, 106
aports of raw stock from, 80-2
escent finishes, 590
a Free State, imports of raw stock from, 80, 83
a moss 480 567 772 moss, 480, 587, 713
(as a measure of thickness), 687, 713
discolorations of tannins, 304 discolorations of tannins, 304 tanning, 435 bark, taunin from, 276 bark, taunin from, 276 bark, taunin from, 275-6 glass, 586, 713 an Africa, import restrictions, 106 ports of raw stock from, 80 protts of raw stock from, 77, 80-2 mains from, 278 a tannin from, 278 , tannin from, 279

J
Jamaica, imports of raw stock from, 77, 80-1, 83-4
Jamba, tannin from, 279
Jamrosa, tannin from, 279
Janus Black (dye), 480
Japan, tannins from, 274-5, 277-8
Japan wax, 589, 713
Japanese ccdar, tannin from, 275
Japanese chestnut, tannin from, 275
Japanese oak, tannin from, 277
Japaned leather, 607-13, 713
Japanning, 607, 609-11
Java plum, tannin from, 276

Jhao, tannin from, 278
Juniperus recurva, tannin from, 277

Kaatigua, tannin from, 279 Kafco finish, 604 Karuci IIIISI, 004
Kahua, tannin from, 278
Kambuata, tannin from, 275
Kangaroo' leathers, chemical composition of, 643
photomicrograph of, 642
properties of, 664, 671, 674, 682, 684
raw stock for, 168
skins, 19
imports of, 84
Karri, tannin from, 276
Kashew nut, tannin from, 274
Keratin, 201, 206-7, 213-4, 231, 713
Kermes oak, tannin from, 277
Kerosene, in degreasing sheepskins, 318
sponging sole leather, 621
Kickers, 431, 713
Kid leathers, chemical composition of, 643
import duties on, 87, 91, 93
properties of, 664, 671, 674, 682, 684
Kidco finish, 600
Kidskins (see goatskins)
Kill bark tannin from 276 Kahua, tannin from, 278 Kidskins (see goatskins) Kili bark, tannin from, 276 Killing floor, 60
Killing wool, 488, 713
Kips, definition of, 16, 713 exports, 79 imports, 78 mports, 75

Kip leather, import duties on, 86

Kiss spots, 329, 713

Kiton dyes, 515

Knee staker, 527-9, 713

Knockers, 60, 713

Knocking pens, 60

Knotted tree, tannin from, 277

Koa tree, tannin from, 274

Kodarsi, tannin from, 275

Koku, tannin from, 274

Korea (see Chosen)

Koreon, 387, 714

Kosher hides, 714

Kyameria triandria, tannin from, 277

Kumbuk, tannin from, 279

Kupaih, tannin from, 275

Kurupaih-ra puihta, tannin from, 277 movement into sight, 75

L

L
Lac dye, 588
Lacca, 588
Lacca, 588
Lace leather, raw stock for, 168
Lacquers, 593-6, 603, 613, 714
emulsion of, 603
LacTan-X, 283, 714
Lactic acid, effect upon plumping, 357-8
in vegetable-tanning extracts, 304
Labrador, imports of raw stocks from, 77, 79,
81, 83-4
Lakes (dye), 591
Lambskins, (see sheepskins)
Laminaria, 587
LaMotte pH comparator, 194-6
photographs of, 195-6
dye indicators, 194
Larch, tannin from, 277
Larix, tannin from various species of, 277
Lasting, effect of kind of tannage on, 692
Latent heat of vaporization, 26, 714
Latvia, imports of raw stock from, 79
Lawras lingue, tannin from, 277
Layaways, 714
Layer vats, 325-7
Laying away, 714
Laying-bye, 67, 714
Leach casting machine, 331-2, 714
Leach house, 286, 330-6, 714
Leaching tanks, 330-3
Leaching vegetable-tanning materials, 281-4, 714

Leather, definition of, 15, 714
Leather finishes, 556-9
Leather gauges, 357, 446, 579
Leatherlubric, 484, 714
Lecithin, 505, 714
Leegers, 60-1, 714
Lemon chrome yellow (pigment), oil-absorption value of, 590
Leucagadagan arganizum tannin from 277 Leuceadendron argenteum, tannin from, 277 Leucospermum conocarpum, tannin from, 277 Leukanol, 320, 388, 414-8, 484, 714 Lice, 115 Licensed warehouse for hides, 144, 714 Licensed weighmasters for hides, 144 Light hides, definition of, 16, 149-50, 714 Lightning buffing machine, 553 Lignins, 283 Lignites, 589 Lignites, 500 Lime, dolomite, 234 hydrated, 234 removal from limed stock by washing, 220 Lime fleshing, 714 Lime liquor, 714 Lime fleshing, 714
Lime liquor, 714
Lime reel, 226
Lime slaking, 714
Limewater, photomicrographs of action on raw stock, 202-5, 213-4
Liming, 201-36
Limitation on delivery against hide contracts, 143
Lining kid leather, finishing, 600
Lining leathers, finishing, 600, 602
raw stock for, 168
Linseed mucilage, effect on ventilating properties of leather, 670
in leather finishes, 566, 587
Linseed-oil varnishes, 607-13
effect on ventilating properties of leather, 671 671 vulcanized, use in waterproofing sole leather, Linum usitatissimum, 587 Lipase, 242, 463, 714 Litharge, in linseed-oil varnishes, 611, 613 Lithophone, oil-absorption value of, 590 Lithuania, imports of raw stock from, 79 627 Littnage, in Inseed-oil Varinishes, 611, 61 Littnophone, oil-absorption value of, 590 Lithuania, imports of raw stock from, 7 Litmus, 194
Live oak, tannin from, 277
Lizard leathers, raw stock for, 168
Locust-bean gum, 587
Logwood, 516, 558, 626, 714
Long-leaved pine, tannin from, 277
Loom-strap leather, raw stock for, 168
Loose leather, 129
Lost hide certificates, 144
Lower California, tannins from, 277
Lowland fir, tannin from, 277
Luggage leathers, raw stock for, 168
Lustrone colors, 604, 714
Luxembourg, import restrictions, 106
Lysiloma candida, tannin from, 277

Macroscopic, 714
Maclura pomifera, tannin from, 277
Macrosporium, 465-6
Madagascar, imports of raw stock from, 77
Madras, import restrictions, 106
imports from, 18
Magenta (dye), 511
Magnetic oxide (pigment), oil-absorption value, 590 390
Mahogany, tannin from, 276
Malachite Green (dye), 512, 515
Malay Archipelago, import restrictions, 106
tannins from, 279, 282
Mallet damage on calfskins, photograph, 126
Malpighia, tannins from various species of, 277
Malpighian layer of epidermis, 203, 212, 715
Maltase 463 Maltase, 463 Mange damage to hides, 116-21, 715 Mangoustan, tannin from, 276 Mangrove, tannin from, 275, 278, 282 (see Cutch extract)

Mangrutta, tannin from, 277
Manna gum, tannin from, 276
Manna wattle, tannin from, 274
Manufacturers' leather, 619, 715
Marking hides for subsequent identification,
170-2
Marsh rosemary, tannin from, 278
Matadero hides, definition of, 17, 715
Materials used in making drums and vats, 393-5
Matrixes for embossing presses, 574, 576, 578,
715
Maul cak tannin from, 277 Mangrutta, tannin from, 277 Maul cak, tannin from, 277 Maxwhite, 486, 599, 715 Measuring area of leather, 580-3 Measuring area of leather, 580-3
Mechanical damage to hides, 108-11
Mechanical leathers, raw stock for, 168
Medicine-ball leathers, import duties on, 87,
Mediterranean coasts, tannin from, 277-8
Mediterranean islands, import restrictions,
Medium chrome yellow (pigment), 588, 590
Melanthrene (dye), 515
Melezitase, 463
Mercuric chloride, 466
Merpol, 715
Mertanol, 418, 715 87, 91 106 Merpol, 715
Mertanol, 418, 715
Mertanol, 418, 715
Messmate, tannin from, 276
Metacresol Purple, 194
Metanitrophenol, 194
Meten leather, raw stock for, 168
Methanol, 715
Methyl red, 194
Methyl violet, 484, 513
Methylene blue, 512, 515
Mexico, imports of raw stock from, 77-80, 83-85
Microorganisms, 186-9, 715
Microscope, 715
Microscope, 715
Microscopic, 715 Microscopic, 715
Micum, tannin from, 276
Mildew, 186
Miljie, tannin from, 274
Milk, use in leather finishes, 584-5
Milling, 438
Milling dyes, 511-3 Milling dyes, 511-3
Mimosa, tannin from various species of, 277
Mineral oils, 507, 625, 715
Minibari, tannin from, 274
Mirbane, oil of, 568, 592
Mixing tank for lime liquors, 227
Moccasin leather, raw stock for, 168
Mocha leather Moccasin leather, raw stock for, 168
Mocha leather, raw stock for, 168
Moellon degras, 432, 491, 507-8, 624, 715
Molds, 71, 186, 454-67, 715
growing in leather, photomicrographs, 454-5
Molle, tannin from, 278
Monel metal, 393-4
Montan wax, 589, 715
Monterey pine, tannin from, 277 Montan wax, 589, 715
Montarey pine, tannin from, 277
Mordant, 715
Mordant Yellow (dye), 484
Morocco, import restrictions, 106
imports of raw stock from, 80-2
tannins from, 278
Morocco leather, 715
raw stock for, 168
Mountain ash, tannin from, 276
Mountain gum, tannin from, 275 Mountain ash, tannin from, 276
Mountain gum, tannin from, 275
Mountain hickory, tannin from, 274
Movement into sight, of raw stock, 75-6
Muccilanceae, 458, 466
Mucilages, use in leather finishes, 586-8
Mucoraccae, 457
Muhurain bark, tannin from, 275
Mulurain bark, tannin from, 275
Muriatic acid, (see hydrochloric acid)
Muscle tissue, 19, 34, 51
Musk, 598
Mycelium, 457
Myrica, tannin from various species of. Myrica, tannin from various species of, 277 Myrobalans, acids in, 304 control of pH value with, 286 cost of, 293

Myrobalans, domestic consumption, 281 extract, imports, 279 fixation value of, 298 imports of, 279 in dyeing, 516 penetrating power of, 298 stability of, 294 sugars in, 304 tannin content of, 279, 282, 292, 293

N

Nance, tannin from, 277
Nangapirih gwazu, tannin from, 276
Naphtha, 568, 609-11, 613, 628
Naphthalene, 715
Nathonal dyes, 515
National dyes, 515
Native hides, definition of, 16, 149, 715
Natural color, 481
Natural dyestuffs, 516, 715
Nauclea gambir, tannin from, 277, 284
Navy Blue (dye), 513, 515
Neatsfoot oil, 470, 483, 490, 669
Needle bark, tannin from, 276
Nemathelminthes, 234
Neolan dyes, 515
Neomerpin, 553, 715
Neradol, 414
Nerve granules, 21 Nance, tannin from, 277 Nerve granules, 21 Nerve papilla, 39, 55 Nerve papilla, 39, 55
Nerves, photomicrograph of, 37
Netherlands and colonies, import restrictions, 106
imports of raw stock from, 18, 77-83
trade agreements, 89
Neutral solution, 715
Neutralizing chrome-tanned stock, 451-2
Neutralizing chrome-tanned stock, 451-2
Neutralizing chrome-tanned stock, 451-8
New Blue (dye), 515
New Caledonia, tannins from, 274-5, 278
New York Hide Exchange, 138
New York Hide Exchange, 138
New Zealand, imports of raw stock from, 77-9, 81-3 81-3 tannins from, 275-7 Nicaragua, imports of raw stock from, 77-8, 83-5 tannins from, 277 trade agreement, 89 Nigeria, import restrictions, 106 Nigeria, import restrictions, 106 imports of raw stock from, 77, 80-1 Nigeria Black (dye), 559 Nigrosine (dye), 514, 558-9, 567, 626 Niter cake, in making sole leather, 619-20 Nitrobenzene, 592 Nomenclature of hides, 16, 18 Nontannins, definition of, 715 Nanco 715 Noncannins, definition of, 715
Nopco, 715
Nopcol, 621
Nopcolene, 621
Nopcowite, 715
North Country carnaula wax, 589
Northern America, tannins from, 274-5, 277-9, 284
Northern Engage tanning from 274-5, 277-9, Northern Europe, tannins from, 274-5, 277 Northern India, tannins from, 277-8 Norway, imports of raw stock from, 77-81, 83-4 Norway spruce, tannin from, 274 Nuclease, 463 Nucleus, 21 Nutricod, 715

0

Oak gum, tannin from, 278
Oak-bark extract, acids in, 304
cost of, 293
domestic consumption, 280
domestic production, 279
fixation value of, 298
imports of, 279
penetrating power of, 298
stability of, 294-6
sugars in, 304

Oak-bark extract, tannin content of, 292-3 at different Baumé readings, 289 Pasting, 543-6, 716 use in dyeing, 516
tannin from, 283
Offal, 716
Offal, 716 Octea, tannin from various species of, 277
Offal, 716
import duties on, 86, 90
Oil of eucalyptus, 566, 592-3, 715
mirbane, 568, 592, 716
sassafras, 592-3, 716
thyme, 592, 716
Oil skirting leather, chemical composition at different depths below grain surface, 644
Oil tanning, 430-3
Oil wheel, 618-20
Oiling off, 716
Oiling shearlings, 487
Oils used in fatliquoring and stuffing, 490
Oil-spreading, 27
Oil-wheeling sole leather, 619-20, 716
Oleic acid, 481, 491, 507
Oleo-stearine, 482
Oilve Brown (dye), 514
Oilve oil, 480
One-bath chrome-tanning materials, 387-8
general properties, 395-407
One-bath process, 363-4, 716
Ooze leather, raw stock for, 168
Open-vat method of leaching, 284-5
Orange chrome yellow (pigment), oil-absorption
value of, 590
Orange mangrove, tannin from, 275
Orange shellac. 588 Orange mangrove, tannin from, 275
Orange shellac, 588
Organ, definition of, 20
Organic pigments, 590
Organic pigments, 590
Organic pigments, 600, 602-5, 716
Orthochrom finish, 600, 602-5, 716
Orthoclear finish, 600, 602-6, 716
Orange, 516, 716
tannin from, 277
Ostrich leather, raw stock for, 168
Osyris, tannin from various species of, 277
Ounce (as a measure of thickness), 446, 716
Overshot buffer, 485, 551-2, 716
Overshot buffer, 485, 551-2, 716
Overweight kip, definition of, 16, 716
Ox, 716 Overweight Kip, deminded Cr., 716
Ox, 716
Ox blood, 558, 586, 605
Oxalic acid, 621, 700
Oxalis gigantea, tannin from, 277
Oxidation of tannins, effect of pH value, 301
Oxidizing agent, 716 Pacific Coast hides, definition of, 17, 150, 716
Pacific post oak, tannin from, 278
Pacific states, tannins from, 274-5, 277-9
Packer hides, definition of, 17, 716
Packing leather, raw stock for, 168
Paddle vats, photographs of, 198, 209, 215, 218
Paddle wheel, portable, 210
Pactilomyces, tannin from, 466
Pagatpat, tannin from, 278
Palspearl, 590, 716
Pakuri, tannin from, 278
Palestine, import restrictions, 106
imports of raw stock from, 77, 80, 82
Palmitic acid spew, 490
Palo blanco, tannin from, 277
Palo rosa, tannin from, 277
Palo rosa, tannin from, 274
Panama, imports of raw stocks from, 83
Pancreol, 716
Panared, 716
Para red (pigment), oil-absorption value of, 590
Parachlor-meta-cresol, 466
Paraffin oil, 480, 486, 507, 607, 628
Paraffin wax, 625-6
Paraguay, import restrictions, 106
imports of raw stock from, 85

Paraguay, import restrictions, 106 imports of raw stock from, 85 tannins from, 274-80 Paranitrophenol, 194, 592, 716 Parasites, hide damage by, 111-24 Parchment leathers, raw stock for, 168 Patchouly, 598
Patent Blue (dye), 512
Patent leathers, 607-13 chemical composition of, 643 chemical composition of, 643 finishing, 607-13 import duties on, 86, 91 photomicrographs of, 610-2 properties of, 664, 671, 674, 682, 684 raw stock for, 168 Pattern of a hide, 59-60, 716 Paullinia sorbilis, tannin from, 277 Paypay, tannin from, 277 Pea wattle, tannin from, 274 Pearl finishes, 590-1 Peccary, 716 Peccary, 716 Peeling pasted leather from plates, 541
Peltophorium dubium, tannin from, 277
Penetrating power of vegetable-tanning materials,
298-300 Penetrating power of vegetable-tanning material 298-300
effect of pH value on, 299
Penetration, 716
Penicillium, 463, 465-6
Pentacme stavis, tannin from, 277
Penta-meta-gigalloyl-beta-glucose, 272
Pepper box, 114-5, 716
Permanganate bleach, 454
Permeability of leather to water vapor, 664-7
Persia, (see Iran)
Peru, import restrictions, 106
imports of raw stock from, 77-8, 80-1, 83-5
tannins from, 275, 277
Petrolatum, 628
pH scale, 192-3
pH value, effect on alum tanning, 418-20
bating, 240-51
Calgon tanning, 423-7
chrome tanning, 470, 484, 486, 500
formaldehyde tanning, 421-2
Leukanol tanning, 417-8
plumping and falling, 256-7
quinone tanning, 435
scoking 197 quinone tanning, 435 soaking, 197 tungstate tanning, 434 vegetable tanning, 352-8 measurement of, colorimetric, 194-6
electrometric, 290-1
Phenol, 591-2
Phenol red, 194
Philippine Islands, import restrictions, 106
imports of raw stock from, 77-8, 82
tannins from, 275, 278-9
Phosphine (dye), 513, 515, 559
Phosphorated oils, 430, 505-7, 716
Phyllanthus emblica, tannin from, 277
Phyllanthus emblica, tannin from, 277
Physical possession of hides without virtual ownership, 136-7, 160
Physical structure of leather, 632-8
Piagao, tannin from, 279
Piano leather, raw stock for, 168
Picca, tannin from various species of, 277
Pickers, rawhide, 630, 634-5, 643
chemical composition of, 643
photomicrograph of, 630
Pickling, 70-1, 265-7, 717
Pigeon manure, use in bating, 237-8
Pigment finishes, 588-9, 566, 717
Pigments, oil-absorption values of, 590
use in leather finishes, 589-91
Pigment-grinding mill, 558
Pigskins, (see hogskins)
Pihkasurembiu, tannin from, 275
Pile-up of leather, 717
Pilling sole-leather crops, photograph, 616
Pilo-motor nerves, 27
Pindo, tannin from, 275
Pine, tannin from, 275
Pine, tannin from, 277
Pin-seal leather, raw stock for, 168
Pinns, tannin from various species of, 277 measurement of, color electrometric, 290-1 colorimetric, 194-6 Pine, tannin from, 277
Pin-seal leather, raw stock for, 168
Pinus, tannin from various species of, 277
Pipey leather, 129-30, 717
Piptadenia, tannin from various species of,
Pistacia, tannin from various species of, 277

Pithecolobium dulce, tannin from, 277 Placing hides in deliverable condition, 155 Placing hides in deliverable condition, Plantation gambier, 284 Plastic, 717 Plasticizers, 558, 594, 717 Plating, 485, 561-2, 579, 717 Plump hides, definition of, 17 Plumping, 256-8 Plunger for mixing liquors, 211 Pneumatic leather, raw stock for, 168 Pocketbook leather, raw stock for, 168 Poland, import restrictions, 106 Poland, import restrictions, 106 imports of raw stock from, 77, 79-80 Polygonum, tannin from various species of, 277 Polyvinyl chloride, 597 Polyvinyl chloride, 597
Pomegranate, tannin from, 277
Pomegranate, tannin from, 277
Por pattern from improper flaying, 125, 717
Poplulus tremula, tannin from, 277
Porsoity of leather, 667-70, 717
Portfolio leathers, finishing, 604
raw stock for, 168
Portugal, import restrictions, 106
imports of raw stock from, 80, 84
Portuguese Africa, import restrictions, 106
imports of raw stock from, 80, 83
Post-mortem changes, 717
Potassium permanganate, bleaching with, 454
Potato-dextrose agar, 459, 462
Pox, 122 Pox, 122 Pratt's Manual, 134 Fratt's Manual, 134
Precipitation test for chrome liquors, 375
Premium grades of hides, 152
Pressing, 315, 438, 717
Press-over system, 296-7, 324-5, 717
Price-fluctuation limitation for hides, 155
Price multiples for hides, 154
Priceks, 21
Prickles, 21
Prickly pear, tannin from 276 Prickles, 21
Prickles pear, tannin from, 276
Primal finish, 600, 603, 605, 717
Pritch pole, 61, 717
Producers, hide, 132
Properties of leather, 629-703, 717
vegetable-tanning materials, 272-305 vegetable-tanning materials, 2/2-305
Prosopis oblonga, tannin from, 277
Protea, tannins from various species of, 277
Protease, 242, 463, 717
Proteins used in leather finishes, 584-6
Protoplasm, 21
Prussian blue (pigment), in linseed-oil varnishes, 610, 613 610, 613
613, 613
oil-absorption value, 590
Pseudotsuga taxifolia, tannin from, 277
Psychrometer, sling, 531
Psychrometer, sling, 531
Psychrometric tables, 533
Psychrometric tables, 533
Psychrometric tables, 533
Psychrometric tables, 571
Psychrometric tables, 571
Pudling, 609
Puer shop, 238, 717
Puering, 237, 717
Pulling a hide pack, 72, 717
Pulling a hide pack, 72, 717
Pump for vegetable-tan liquors, 334
Pump logs, 308, 717
Purchasing hides and skins, 170-99
Purity of vegetable-tanning materials, 717
Putterfaction, 71, 129-30, 186
Putting out, (see setting out)
Psyropissite, 589
Pyroxylin, 593-8, 717 Quandony, tannin from, 276 Quebrachia lorentzii, tannin from, 277, 280-1

Quandony, tannin from, 276
Quebrachia lorentzii, tannin from, 277, 280-1
Quebracho extract,
acids in, 304
bisulfiting, 288
cost of, 293
domestic consumption, 280
effect of pH value on precipitation of, 302-3
fixation value of, 298-300
imports of, 279
method of preparation, 280-1
penetrating power of, 298-300

Quebracho extract, stability, 294-6 sugars in, 304 tannin content of, 292-3 at different Baumé readings, 289 use in dyeing, 516 Queensland, tannins from, 274-5 Quercitron bark, 516, 717 Quercus, tannin from various species of, 277-8, 282-3 Quinone, 718 Quirone, 718 Quirone, 718 Quirone tanning, 434-5 Quiron tanning, 439, 486, 488-9, 615 Quotations for hides, committee on, 139

ĸ

Raffinase, 463
Randall & Stickney gauge, 357
Raspberry jam wood, tannin from, 274
Raw sienna (pigment), oil-absorption value of, 590
Raw umber, in linseed-oil varnishes, 609, 611 Rayox, 718 Rayox, 718
Razor-strop leather, raw stock for, 168
Recording hygrometer, 533
Red alder, tannin from, 274
Red cebil, tannin from, 274
Red gum, tannin from, 276
Red iron bark, tannin from, 276 Red iron bark, tannin from, 276
Red mallet, tannin from, 276
Red mangrove, tannin from, 275
Red oak, tannin from, 278
Red pine, tannin from, 278
Red pine, tannin from, 277
Red wattle, tannin from, 277
Red wattle, tannin from, 277
Reducing agent, 364, 718
Redwood, tannin from, 278
Redwood, use in making drums and vats, 393
Reeling, 226-7
Relative humidity, 530-9, 718
effect upon chamoising, 433
drying of leather, 540-2
properties of leather, 655-9, 666-7, 671-8, 685-6, 700
tables, 534-9, 718
Rennet, 463
Reptile leather, import duties on, 87, 92
raw stock for, 168
skins, imports of, 83
Residue, 718
Resilience of leather, 683-6, 718 Red mallet, tannin from, 276 Resilience of leather, 683-6, 718 Resins, use in leather finishes, natural, 588 synthetic, 593-8 Resorcine Brown (dye), 480-1, 484, 513, 515 Restricted-import countries, 106, 718 Reticular layer, 30, 32, 718
Reticulin, 39, 718
Reticulin, 39, 718
Rhatany, tannin from, 277
Rheedia brasiliensis, tannin from, 278 Rhizophora, tannin from various species of, 278, 282 Rhodamine (dye), 515 Rhus, tannin from various species of, 278, 284, 589 Ribbon gum, tannin from, 275
Rinderpest, 106
Ringworm scars, 123-4
Rinse liquor, 615
Rinsing, 615, 617
Robinia pseudacacia, tannin from, 278
Rocceline (dye), 515
Rock salt, use in curing, 63
Rocker yard, 323-5
Roller leather, raw stock for, 168
Rolling leather, 569-70, 621-2, 626, 718
Rolling leather, 569-70, 621-2, 626, 718
Rollinia, tannin from, 278
Rosin, 588, 607, 718
Rough-barked apple, tannin from, 274
Round-belting leather, 168
Round-leaf moort, tannin from, 276 Round-leaf moort, tannin from, 276 Rubber latex, use in leather finishes, 593, 603, 718 Rubber beds, 579 bolsters, 579 rolls, 451 Rumania, import restrictions, 106 imports of raw stock from, 80

Rumex, tannin from various species of, 278 Rumpers, 60-1, 718
Rumpers, 60-1, 718
Run pelts, 234, 718
Russet side leather, chemical composition at different depths below grain surface, 644
Russia (see Union of Soviet Socialist Republics)
Russia calf leather, 16, 598, 718

Sabal, tannin from various species of, 278 Sabdal, tannin from various species of Saddle leather, finishing, 607, 627 import duties on, 86, 90 raw stock for, 168 Safranine (dye), 484, 511, 515, 559 Sal bark, tannin from, 278 Saladero hides, definition of, 17, 718 Salai bark, tannin from, 275 Salix tannin from various species of Salia bark, tannin from, 2/5
Salix, tannin from various species of, 278
Salmon gum, tannin from, 276
Salmon skin, grain pattern of, 57
Salometer, 264-7, 718
Salophilic bacteria, 69
Salova, 485 Salt (see under various operations)
Salt stains, 126-9, 718
Salt thrower, 64, 718
Salvador, imports of raw stock from, 83 Salt thrower, 64, 718
Salvador, imports of raw stock from, 83
trade agreement, 89
Samming, 521-3, 718
Sandalwood oil, 598
Sanitary control of imports, 96-107
Sansafras, oil of, 592.719
Sassafras, oil of, 592.3
Saturated air, 528-30, 719
Saudi Arabia, import restrictions, 106
imports of raw stock from, 79-81
Saw palmetto, tannin from, 278
Sawdust, use in samming, 522-3
Scabies, 120-1, 719
Scalp, 25
Scar tissue, 33, 114
Scarlet oak, tannin from, 277
Schimus molle, tannin from, 278
Schizophyta, 187
Scotted hides, 125, 719
Scott fir, tannin from, 277
Scott grain, 719
Scott fersile-strength machine, 647, 691
Scratches on hides, 108-9
Scudding, 217-20, 260, 719 Scott tensile-strength machine, 647, 691
Scratches on hides, 108-9
Scudding, 217-20, 260, 719
Sealskin leather, raw stock for, 168
Sealskins, imports of, 84
Seasonal differences in raw stock, 17, 37
Seasonal period of take-off, definition of, 17
price adjustment for, 152
Seasoning machine, 550, 626
Seat-cover leather, raw stock for, 168
Sebaceous glands, 27-8, 40-3, 202-5, 719
Sebum, 719
Sebum, 719
Selection factors for hides, 151, 719 Selection factors for hides, 151, 719 Selection of hides for specific leathers, 166-9 Septa, 457 Sequoia sempervirens, tannin from, 278
Sequoia sempervirens, tannin from, 278
Serial-table putting-out machine, 474
Setting-out cylinders, 451
Setting-out leather, 439-44, 474-7, 620, 625, 719
Sex, effect upon quality of raw stock, 16
Shanki, 719
Shanking ovlinder, 452 Shanking cylinder, 452 machine, 475 Shark leather, 92, 168, 638, 642-3, 671, 674, 682, Sharkskins, imports of, 84
Sharpening agents in liming, 222-3, 719
Shaved weight, 451, 719
Shaving cylinder, 452
leather, 447-50
machines, 442-3, 448-52, 719
Shearling leathers, 168, 385-7, 486, 643, 664, 719
Shearling photomicrographs of 48-9, 52, 232-3 Sheepskins, photomicrographs of, 48-9, 52, 232-3, 249, 319, 381, 387, 635 (see under all appropriate chapter headings)

Sheep wool, photomicrograph of segment of, 49 Shell, 719
Shell cordovan, 53, 384, 641
Shellac, 557, 566, 588, 670, 719
Sheridan press, 574-8
Shipping damage to hides, 130
Shirlan, 719
Sheepunger leather, row stock for 160 Shoe-upper leather, raw stock for, 169
Shorea, tannin from various species of, 278
Shoulder, definition of, 614, 719
Shrink temperature of leather, 418, 421-2, 432,
719 Shrink temperature of leather, 418, 4719
Shrinkage in curing, 63-4, 69-70
Siam (see Thailand)
Sicily, tannins from, 278, 284
Side, definition of, 719
Side floorsmen, 60
Sig water, 719
Silica tanning, 435
Silver finishes, 590
Silver fir, tannin from, 274
Silver leather, finishing, 607
import duties on, 87
Silver mallet, tannin from, 276
Silver tree, tannin from, 277
Silver wattle, tannin from, 274
Silver-leaved wattle, tannin from, 275
Silver-leaved wattle, tannin from, 275
Sitka spruce, tannin from, 277
Silver-leaved wattle, tannin from, 275
Sikin definition of, 16, 719
Skin definition of, 16, 719
Skining bed, 61
Skiriting leather, raw stock for, 169
Skivers, 416, 431, 719
raw stock for, 169
Slack tanning, 719
Slaughter, 60
Slicking, 476, 477, 626, 719 tanning for white leather, 390
Slack tanning, 719
Slaughter, 60
Slicking, 476, 477, 626, 719
Sliing psychrometer, 531, 719
Small-packer hides, definition of, 17, 59, 719
Smooth-barked apple, tannin from, 274
Smoothplating, 485, 561, 562, 579
Snakeweed, tannin from, 277
Snow bush, tannin from, 275
Snuffing, 719
Soak fleshing, 720
Soaking raw stock, 176-182, 191, 196-200, 720
Soaps, 491, 720
Soaps, 491, 720
Socoerball leather, import duties on, 87, 91
Sodiam sliftuoride, 106, 720
Sodium alginate, 587
Sodium chloride (common salt), (see under various operations)
Sodium chloride (common salt), (see under various operations) ous operations)
Sodium cyanide, 223, 720
Sodium dichromate, 363-8
Sodium formate, 391-2, 402, 420, 720
Sodium hydrosulfide, 207-31, 720 Sodium metaphosphate, 422-27, 720 Sodium nitrite, 485 Sodium okate, 487, 491 Sodium oxalate, 402-3 Sodium pentachlorphenate, 466 Sodium permanganate, 720 Sodium phenolate, 591 Sodium pilenoiate, 591
Sodium silicate, 435
Sodium silicofluoride, 106
Sodium sulfate (see under various operations)
Sodium sulfide, 207-31, 720
Sodium thiosulfate, 363
Sodium tripherphate, 424 Sodium triphosphate, 424 Sodium tungstate, 434, 720 Solcod, 720 Sole leather, 86, 90, 169, 225-8, 322-39, 614-28, 643, 664, 671, 674, 684, 687-90
Sol-Neats, 720 Solubility of water in air, 528-39 Solvents, lacquer, 594 Somaliland, import restrictions, 106 tannins from, 274

Stuffing leathers, 468-509, 625, 721 Stuffing mill, 481 Stunted wattle, tannin from, 274 Sonneratia pagatpat, tannin from, 278 Sour dip for sole leather, 621, 720 South Africa, tannins from, 277 South American hides, 70 Stunted wattle, tannin from, 274
Styrax, 598
Sucking lice, 115
Sudan, tannin from, 274, 276-7, 279
Sudoriferous glands, 25, 26, 44, 721
Suède leather, 169, 485, 551-3, 637, 639, 643, 664, 671, 674, 682
Sugarbush, tannin from, 277
Sugar gum, tannin from, 276
Sugars, in making chrome liquor, 364
in sole leather, danger of excessive amounts, 627
in vegetable-tanning materials, 304
Sulfides, 207-31
Sulfite cellulose (see Spruce extract) South American hides, 70
Spain, import restrictions, 106
imports of raw stock from, 80, 82
Spanish chestnut, tannin from, 275
Specific gravity, apparent of leather, 705
of liquids, conversion tables, 265, 288
Specific heat, 26, 720
Specifications for deliverable hides, 147-50
Speculation, effect on hide market, 161
in hides, 136-7, 160, 162-3
Spent das bark, demand for, 283
Spent tan, 720
Spermolepsis gummifera, tannin from, 278
Spews, 490, 720
Splenic fever, 115
Splits, 720
chemical composition of, 643 Sulfides, 207-31
Sulfite cellulose (see Spruce extract)
Sulfo-glyconeats, 484
Sulfonated castor oil, 485, 558
coconut oil, 388, 430
cod oil, 481, 590, 620, 624
linseed oil, 558, 599, 605
neatsfoot oil, 469-70, 478, 483, 487, 496-501
oils, 495-501, 590, 670, 721
Sulfur dioxide, 364-8, 721
Sulfur monochloride, 568, 627
Sulfuric acid, destructive action on leather, 694700 Splits, 720
chemical composition of, 643
import duties on, 86, 90
strength of, 664
Splitting, 443-7, 720
effect on properties of leather, 651-4
Splitting horse, 322, 720
Splitting machine, 445-7, 720
Sporangium, 457
Spot hides, 721
Spot tradine, 137 700 use in bleaching vegetable-tanned leather, 452-4, 617-8
Calgon tanning, 423-30
deliming, 239-40, 258
fatliquoring, 470, 484
pickling, 265-7
plumping, 358
Sumac, cost of, 293
domestic consumption, 26
domestic production, 279
imports of, 279
in dyeing, 478-9, 516
stability of, 294
stainless, 484
tannin content of, 278, 2 617-8 Sportings with teachers, 1981, 121
Sportings with, 457
Spot hides, 721
Spot hides, 721
Spot tading, 137
Spotted gum, tannin from, 275-6
Spray finishing, 571, 721
Spreading of oils, 468, 721
Spreads, 67-8
Spready hides, definition of, 17, 721
Spruce extract, cost of, 293
domestic consumption, 280
fixation value of, 298
in vegetable-tanning, 309, 316
penetrating power of, 298
preparation of, 283
stability of, 294
tannin content of, 292-3
Stability of vegetable-tanning materials, 294-6
Stag hide, definition of, 16, 721
Staking, 523-6, 540-2, 561, 570, 721
machines, 524-5, 529
Standard quality of hides, 147
Staphylococci, 189, 721
Starche gum, 588
Starches in finishing, 588, 670
Statice coriaria, tannin from, 278
Stearine, 625
Steerhide, definition of, 16, 721
Steerhides, photomicrographs of, 111-3, 116-8, 339, 383, 623, 626, 629, 632-3
(see under all appropriate chapter headings)
Stephanofilariasis, 121-2
Sterigmata, 458, 466
Stick lac, 588
Stick vats, 307-15, 721
Stickers, 60, 721 tannin content of, 278, 284, 292-3 Sundri bark, tannin from, 276 Sungra katus, tannin from, 278
Sunning patent leather, 613, 721
Superficial fascia, 19, 721
Super-spruce extract, 283, 721
Surface tension, 721
Suspender-strap leather, raw stock for, 169
Swabbing, 558, 721
Swamp gimlet, tannin from, 276
Swamp pine, tannin from, 277
Sweat chamber, 231, 721
Sweat glands, 25-6, 44, 721
Sweating, 231-4, 722
Sweden, import restriction, 106
imports of raw stock from, 77-9, 82-3
trade agreement, 89
Sweet fern, tannin from, 277
Swelling, 722
Switzerland, import restrictions, 106
imports of raw stock from, 77-80, 83
trade agreement, 89
Sweet forn, tannin from, 277 Sungra katus, tannin from, 278 imports of raw stock from, 7/-8 trade agreement, 89
Synektan, 418, 722
Syntans, 414-18, 722
Synthesis, 722
Synthetic resins, 593-8
Syria, import restrictions, 106
imports of raw stock from, 80 Stick vats, 307-15, 721 Stickers, 60, 721 Sticking piece, 60-1, 721 Stilbaceae, 458 Sticking piece, 60-1, 721
Stilbaceae, 458
Stirrup leather, raw stock for, 169
Stock liquor, 309, 721
Stock rooms for leather, 585-6
Stone age, leather from, 272
Storage of certificated hides, 144
Storage tanks, 330
Straight hair, cause of, 50
Straits Settlement, import restrictions, 106
Strap leather, finishing, 627
import duties on, 87, 91
raw stock for, 169
Strength of leather, 645-64
Streptocacci, 189, 721
Stretch of leather, 645-64
Stript, hogskin, 19, 77-8
Stryphnodendron barbatimao, tannin from, 278
Stuffing greases, 507, 625 Tabique, tannin from, 279
Tacking leather, 479, 519, 526, 722
Tacky, 722
Tacky finish, 605
Tail vat, 324, 722
Tail-pullers, 60-1, 722
Take-off, standard of, 148, 722
Take-up of hides, 148
Talh, tannin from, 274 Talh, tannin from, 274
Tallow, 482, 625
Tamarisk, tannin from, 278
Tamariz, tannin from various species of, 278
Tamol, 416, 483-4, 722

Tamwood, tannin from, 275 Tan-liquor heater and cooler, 335	Trehalase, 463
Tan-liquor heater and cooler, 335	Trianol dyes, 511-14
Tanak, 418 Tanasol, 418, 722	Triazol Brown (dve), 515
Tanbark oak, tannin from, 277	Trichilia, tannin from various species of, 279 Trichlandlamine, 481, 507, 723 Trim of libes, 148
Tangal, tannin from 275	Triemanolamine, 481, 507, 723
Tangal, tannin from, 275 Tanigan, 389, 417, 722 Tannase, 303, 463, 464	Trimming leather 566 568 570 723
Tannase, 303, 463, 464	Trimming leather, 566, 568, 570, 723 raw stock, 176-7
Tannin, definition of, 722	1 riton, 553, 723
errors in analysis of, 291	True skin, 19, 20, 23, 723 Trypsin, 39, 242, 723
strengths of liquors at different degrees	Trypsin, 39, 242, 723
Baumé, 289 Tannins, 272-305	Tsuga, tannin from various species of, 279, 284 Tuberculariaceae, 458
distribution through thickness of leather, 347	Tungeten tanning 424
	Tungsten tanning, 434 Tunisia, import restrictions, 106
Temper of leather, 679-83, 722	imports of raw stock from, 80, 83, 85
Tanoyl, 430, 470, 473, 484, 486, 505, 722	Turkey, import restrictions, 106
Temper of leather, 679-83, 722 Tanoyl, 430, 470, 473, 484, 486, 505, 722 Tapia gwazu-ih, tannin from, 274 Taps, import duties on, 86, 90	imports of raw stock from, 80, 82
Taps, import duties on, 60, 90	tannins from, 278
Tara pods, tannin from, 275 Tare allowance, 722	Turkey oak, tannin from, 277 Turner thickness gauge, 446
Tariff act, 86-96	Tutu, tannin from, 275
Tartar emetic, 478-9, 722	Twaddell hydrometer, 288, 723 conversion tables, 288
Tartrazine (dye), 512	_ conversion tables, 288
Tarwar, tannin from, 275	I Wo-path process, 363, 723
Tasmania, tannins from, 277 Tawing, 418, 722 Tawing, 418, 722	Two-toning, 605
Taxis cuspidata, tannin from, 278	· ·
Tea, tannin from, 275	Ū
Tearing resistance of leathers, 654, 663-4, 723	Ultramarine (pigment), oil-absorption value of,
Temper of leather, 679-83, 722	590
Temperature control of animal body, 25-30	Umbellularia californica, tannin from, 279
Temperature, effect of (see under various operations)	Unctious, 723 Unglazed wax enamel leather, finishing, 602 Unhairing, 201-36 machines, 212, 215, 224 Unhairing cylinders, 451
Tempering sole leather, 616-7, 722	Ungrazed wax enamer reatner, nurshing, 602
Tenderable grades of hides, 146	machines 212 215 224
Tensile strength of leather, 645-64, 722	Unhairing cylinders, 451
Tergitol, 722	Union of South Africa, import restrictions, 106
Terminalia, tannin from various species of, 278-9,	imports of raw stock from, 77-82, 85
282 Tomas famous 115	Unhairing cylinders, 451 Union of South Africa, import restrictions, 106 imports of raw stock from, 77-82, 85 Union of Soviet Socialist Republics, import re-
Texas fever, 115 Texas steerhides, definition of, 16-7, 149, 722	strictions, 100
Textile leather, raw stock for, 169	strictions, 106 tannins from, 274, 278 United Kingdom, imports of raw stock from, 18, 77-9, 81-3, 85
Textile leather, raw stock for, 169 Thailand, import restrictions, 106	77-9, 81-3, 85
imports of raw stock from, 79, 82-3 Thallophyta, 187, 722 Thann, tannin from, 279 Thann, tannin from, 279	trade agreement, 89 Unloading hides at tannery, 171 Upholstery leather, finishing, 604 import duties on, 87
Thallophyta, 187, 722	Unloading hides at tannery, 171
Thann, tannin from, 279	Upholstery leather, finishing, 604
	import duties on, 8/
Thermostat layer, 23, 25, 48, 722	raw stock for, 169 Urea, 723
Thermostat, 722 Thermostat layer, 23, 25, 48, 722 Thickness of leather over area of calfskin, 645-8	Urease, 463
Thickness of leather over area of calfskin, 645-8 of various satisfactory leathers, 664 Thorny wattle, tannin from, 274 Three-arm staker, 486-7, 722 Thyme, oil of, 592 Thymol Blue, 194 Thymus valoaris, 592	Uruguay, import restrictions, 106
Thorny wattle, tannin from, 274	imports of raw stock from, 77-9, 81-3, 85
Three-arm staker, 486-7, 722	
Thyme, on or, 592 Thymol Blue 104	V
Thymus vulgaris, 592	Vacuum evaporator, 281, 723
Thymus vulgaris, 592 Ticks, 115-6 Timbe towin from 275	Valonia, acids in, 304
	Vacuum evaporator, 281, 723 Valonia, acids in, 304 cost of, 293
Time, effect of (see under various operations) Tin crystals, 722 Ti-Pure, 389, 722 Ti-Pure, 389, 722	domestic consumption, 280
Tin Crystals, 722	fixation value, 298 imports, 279
Tissue definition of 20	nenetrating nower of 298
Tissue, definition of, 20 Titanium dioxide, 388-90, 590, 722	penetrating power of, 298 stability of, 294
Titanium potassium oxalate, 484 Titanox, 388, 722 Title to hides, 156 Tizra sumac, tannin from, 278 Toggle, 722	tannin content of, 277, 282, 292-3
Titanox, 388, 722	use in dyeing, 516
Title to hides, 156	Valve leathers, raw stock for, 169
Torgle 722	Van Dyke Brown (pigment), oil-absorption value
Toggling 490 526-8 723	of, 590 Varnish coat, 613, 723
Toggling, 490, 526-8, 723 Toluene, 594	Vaseline, 482
Toner Brown (pigment), oil-absorption value of,	Vat. 723
590	Vateria indica, tannin from, 279 Vegetable gum, 588
Toner Yellow (pigment), oil-absorption value of,	Vegetable gum, 588
590 Tooling leather, 574 723	Vegetable tanning, 306-62, 723 materials, 272-305
Top buffing, 553	Veins, 34
Tooling leather, 574, 723 Top buffing, 553 Top finish, 723	Veins, 34 Veiny leather, 127, 129, 723 Venezian finish 485
Tormentilla erecta, tannin from, 279	Venecian finish, 485 Venetian sumac, tannin from, 278
Trace agreements, 87, 89	Venetian sumac, tannin from, 278
Tragasol 419 430 587 723	Venezuela, imports of raw stock from, 77, 80-1, 83-5
Tormentilla erecta, tannin from, 279 Trade agreements, 87, 89 Tragacanth, 587, 723 Tragasol, 419, 430, 587, 723 Transfer of certificated hides, 144 Transferable notice for hides, 156	tannins from, 279
	Ventilating properties of leather, 663-71 Vici kid, 723
Transvaal, tannins from, 277	Vici kid, 723

Victoria Violet (dye), 513, 515 Vinylite resin, 723 Virginian sumac, tannin from, 278 Virtual ownership of hides, 136-7, 160 Viscols, 568, 723 Vitriol, oil of (see sulfuric acid) Voids in leather, 723 Volleyball leather, raw stock for, 169 Vulcanized oils, 568, 627

W

Waist-belt leather, raw stock for, 169
Wallaby skins, 19
imports of, 84
Wallaby leather, raw stock for, 169
Wallet leather, raw stock for, 169
Walrus leather, import duties on, 92
Wandoo, tannin from, 276
Warble fly, 111-5
Warehouse receipts for hides, 144
Warehousing for hides, committeee on, 139
Warm-water pool, 228, 723
Warsts, 124, 723
Washer leathers, raw stock for, 169
Washing leather, (see under various operat Washing leather, (see under various operations) raw stock, 179-81, 219 Water content of leather, effect of relative humidity, 672-4, 685 Water for tannery use, 185-6 Water oak, tannin from, 278 Water buffalo leather, 636 Waterless moellon, 480, 482
Waterproofing sole leather, 627-8
Wattle bark, acids in, 304
cost of, 293
domestic consumption, 281 consesse consumption, 281 fixation value, 298, 300 imports, 279 penetrating power of, 298, 300 stability of, 294-6 sugars in, 304 sugars in, 304 tannin content of, 282, 292-3 use in dyeing, 516 Waxes, use in leather finishes, 588-9, 670 Wear resistance of leather, 685-90 Wearing blue transit fore, 277 Wear resistance of leather, 685-90
Weeping blue, tannin from, 277
Weeping willow, tannin from, 274
Weighing hides as received at tannery, 170-1
Weimannia glabra, tannin from, 279
Welting leather, import duties on, 86, 90
raw stock for, 169
Western chingwood, tannin from, 275 Western hemlock, tannin from, 279 Western larch, tannin from, 277
Wet-and-dry bulb thermometer, 531-3, 724
Wet shaver, 443 Wetting agent, 724 Wheel, 724 Wheel, 724
Wheeling, 438, 724
Whip leather, raw stock for, 169
White birch, tannin from, 275
White box, tannin from, 276 White carnauba wax, 589 White connective tissue, 36-7 White elk side leather, finishing, 600 White fatliquor, 486 White kid leather, 637, 643, 664

White leathers, 388-90, 429-30, 486, 599-600
White mallet, tannin from, 276
White mangrove, tannin from, 274
White oak, tannin from, 277-8
White oak, tannin from, 277-8
White sheep pouch bag leather, finishing, 600
White shellac, 588
White spruce, tannin from, 274
White shellac, 588
White spruce, tannin from, 278
White simac, tannin from, 278
White millow, tannin from, 278
White millow, tannin from, 278
White willow, tannin from, 278
White willow, tannin from, 278
Whitening cylinder, 452
Whitening cylinder, 452
Whitening wachine, 625
White suede leather, fatliquoring, 486
Wild grain (see marbled grain)
Wild willow, tannin from, 274
Willow, tannin from, 278
Willow, tannin from, 274
Willow, tannin from, 274
Wilson-Kern method of tannin analysis, 292
Wire damage to hides, 109-11
Woburn thickness gauge, 579
Wooden horse, 72, 268, 472, 713
Woodfordia floribunda, tannin from, 279
Wool-clipping machine, 488, 724
Wool grease, 482
Wool-pullers, 231, 724
Wool yiolet (dye), 484
Woolly-butt, tannin from, 276
Workshoe-upper leather, 637-8
Workshoe-upper leather, 480, 643, 664, 671, 674, 682, 684
Wringing leather, 438-41, 619, 724
Wringing machines, 439-40, 619
Wrist-watch strap leather, raw stock for, 169

X

Ximenia americana, tannin from, 279 Xylia dolabriformis, tannin from, 279 Xylocarpus, tannin from various species of, 279

v

Yaguarataih, tannin from, 275
Yards, 307, 313, 343, 369-71, 378, 382, 724
Yarran, tannin from, 274
Yeasts, 186, 303, 621
Yellow connective tissue, 36-7
Yellow willow, tannin from, 278
Yew, tannin from, 278
Yhsapih-ih, tannin from, 275
Yhva-iha, tannin from, 277
Yhva-jhay puihta gwazu, tannin from, 276
Yhva-viyu, tannin from, 276
Yhva-viyu, tannin from, 276
Yhvihra-pere, tannin from, 277
Yield of leather, 724
Yon, tannin from, 274
York gun, tannin from, 276
Yugoslavia, import restrictions, 106
imports of raw stock from, 78-81, 85
Yukeri gwazu, tannin from, 277

Z

Zymase, 463 Zisyphus, tannin from various species of, 279